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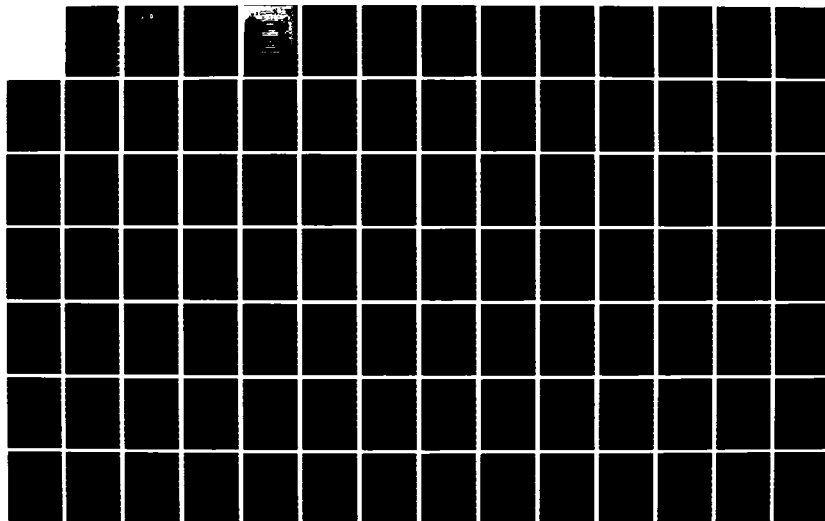
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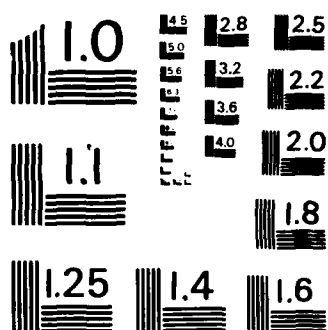
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Two-phase systems of a liquid hydrocarbon mixture, containing medium molecular weight aromatic and aliphatic hydrocarbons, and water were examined in both equilibrium and kinetic experiments. Knowledge of the aqueous solution behavior of liquid hydrocarbon mixtures is important in determining the fate of hydrocarbon components of fuels and petroleum in environmental release situations. Hydrocarbon phase activity coefficients determined for binary hydrocarbon mixtures using static vapor pressure measurements (at 20 and 70

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degrees) and those determined using water solubility results (at 20 and 70 degrees) did not differ significantly. This indicated that component aqueous phase activity coefficients did not decrease measurably in the presence of hydrocarbon co-solutes, in contradiction to some previously published observations, and that the presence of water in the hydrocarbon phase was not significant at these temperatures. Methods for predicting multicomponent mixture solubilities were demonstrated. FINAL REPORT, Investigation of Deviations from Ideality in the Two Liquid Phase Region of Systems of Medium Molecular Weight Hydrocarbon Mixtures and Water, AFOSR-83-0036.

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ABSTRACT

Two-phase systems of a liquid hydrocarbon mixture, containing medium molecular weight aromatic and aliphatic hydrocarbons, and water were examined in both equilibrium and kinetic experiments. Knowledge of the aqueous solution behavior of liquid hydrocarbon mixtures is important in determining the fate of hydrocarbon components of fuels and petroleum in environmental release situations.

The equilibrium solute concentration for a component is given by the product of the pure compound solubility, its mole fraction in the hydrocarbon phase and its activity coefficient in the hydrocarbon phase.

Hydrocarbon phase activity coefficients determined for binary hydrocarbon mixtures using static vapor pressure measurements (at 20 and 70°C) and those determined using water solubility results (at 20 and 70°C) did not differ significantly. This indicated that component aqueous phase activity coefficients did not decrease measurably in the presence of hydrocarbon co-solutes, in contradiction to some previously published observations, and that the presence of water in the hydrocarbon phase was not significant at these temperatures. Methods for predicting multicomponent mixture solubilities were demonstrated. Aqueous solution behavior of mixtures containing a chlorinated hydrocarbon or a fatty acid surfactant was also determined.

OBJECTIVES

This research on solution of liquid hydrocarbon mixtures in water was directed to several objectives:

- (a) Determination of the magnitude of solute-solute interactions for pairs of hydrocarbon solutes in the aqueous phase, using solubility and vapor pressure data taken at 20° and 70°C.
- (b) Correlation of molecular structure with water solubility of a number of different aliphatic and/or aromatic binary hydrocarbon pairs.
- (c) Development of methods for prediction of multicomponent hydrocarbon mixture solubility in water, using a twelve component example containing compounds occurring in fuels.
- (d) Measurement of the effect of dissolved salt and natural organic material on the solubility of binary mixtures of hydrocarbons in water.
- (e) Observation, analysis, and modeling of the solution kinetics of hydrocarbon mixtures in water, in closed systems, and in systems with evaporative loss of hydrocarbons.
- (f) Determination of the effect of the presence of a chlorinated hydrocarbon and an alkanolic acid in a hydrocarbon phase on solubility behavior of the hydrocarbon phase components.

GENERAL INTRODUCTION

1. Introduction

Two-phase systems of a liquid hydrocarbon mixture in contact with water are encountered in a variety of environmental and geological situations. Knowledge of the aqueous solution behavior of liquid hydrocarbon mixtures is of importance in determining the fate of hydrocarbon components in such systems.

Petroleum is primarily a liquid mixture of hydrocarbons. Petroleum discharges in the aquatic environment are of particular concern with respect to metabolism by and toxicity to biota. Knowledge of the dissolution process in conjunction with other processes (i.e. evaporation, advection, dispersion, oxidation, sediment interactions and microbial degradation) can help in determining the exposure of biota to petroleum-derived contaminants.

Subterranean situations exist in which a petroleum discharge creates a lens of oil on top of the water table. Sediment-water-contaminant interactions occurring in conjunction with the dissolution process are of particular importance in attempting to understand the fate of petroleum components in ground water.

The composition of a reservoir oil may change due to component dissolution into an associated water phase. Some current theories of petroleum migration from the source rock to the reservoir rock include water as the transport medium. Knowledge of the aqueous solution behavior of hydrocarbon mixtures, in conjunction with sediment interactions, may be of importance in these cases.

Considerable effort has been made to determine the aqueous solubilities of single hydrocarbons (McAuliffe, 1966; Sutton and Calder, 1975; Price, 1976; Mackay and Shiu, 1977; 1981; May, 1978; Whitehouse, 1984; among others). Single compound solubility of a hydrocarbon may not be sufficient to determine its solubility when it is part of a mixture. Solid mixtures of hydrocarbons (or organics, in general) tend to yield component solute concentrations that are the same as the single compound solubility (Eganhouse and Calder, 1976; Banerjee, 1984). A mixture of solid hydrocarbons is, however, a different thermodynamic system than a mixture of liquid hydrocarbons. An examination of the aqueous solubility behavior of mixtures of solid hydrocarbons would add little to an understanding of the aqueous solubility behavior of liquid mixtures of hydrocarbons such as petroleum.

The aqueous solubilities of some liquid binary mixtures of hydrocarbons (or organics, in general) have been examined by Leinonen and Mackay (1973), Green and Frank (1979), Tewari et al. (1982) and Banerjee (1984). Leinonen (1976) examined the aqueous solubility of more complex mixtures of hydrocarbons. The common observation of the above authors was that the aqueous solubility of a component of a liquid mixture was related to its pure compound solubility, the mole fraction of that component in the hydrocarbon (or organic) phase and its activity coefficient in the hydrocarbon (or organic) phase.

Leinonen and Mackay (1973) and Leinonen (1976) also stated that they observed a significant reduction in the hydrocarbon component activity coefficients in the aqueous phase. A reduction in the aqueous phase activity coefficient would have a positive effect on solubility.

Such observations, if correct, may indicate significant hydrophobic interactions and have considerable implications as to the role of water as a solvent for hydrophobic molecules. Green and Frank (1979) did not observe a reduction in the aqueous phase activity coefficient.

A major purpose of the present study was to further examine the equilibrium aqueous solubility behavior of liquid hydrocarbon mixtures and determine if a reduction in the hydrocarbon activity coefficient in the aqueous phase can be detected within the precision of water solubility measurements.

2. Review of Literature

Water is a unique liquid with many anomalous properties. Water is structured, and reviews of various water structure theories have been given by Horne (1968) and Ben-Naim (1974), among others. Most recent theories suggest that in order for hydrophobic molecules such as hydrocarbons to dissolve in water, cavities or "holes" in highly structured water are created to accommodate the non-polar molecules and isolate them from the bulk water.

Water is a very strongly and regularly hydrogen bonded liquid, which accounts for many of its anomalous properties, as well as for many of the difficulties encountered in establishing an adequate quantitative theory of liquid water or aqueous solutions of non-electrolytes. "No one has yet proposed a quantitative theory of aqueous solutions of non-electrolytes, and such solutions will probably be the last to be understood fully." (page 174, Rowlinson and Swinton, 1982). Since no adequate theory is available, an understanding of aqueous solutions of non-electrolytes may best be gained through experimental observations.

The first detailed study of the aqueous solubility of liquid hydrocarbon mixtures was reported by Leinonen and Mackay (1973), who examined the aqueous solubility of binary hydrocarbon systems containing cyclohexane and benzene with each of n-hexane, 1-hexene and 2-methylpentane at 25°C. They derived the following relationship based upon the thermodynamics of a two phase water-hydrocarbon system:

$$x_{i(w)} = x_{i(h)} \gamma_{i(h)} \frac{1}{\gamma_{i(w)}} \quad (1)$$

, where $x_{i(w)}$ is the mole fraction of component i in the aqueous phase, $x_{i(h)}$ is the mole fraction of component i in the hydrocarbon phase, $\gamma_{i(h)}$ is the activity coefficient of component i in the hydrocarbon phase and $\gamma_{i(w)}$ is the aqueous phase activity coefficient of component i. Assuming $\gamma_{i(w)}$ is not reduced by the presence of other hydrocarbon cosolutes, $1/\gamma_{i(w)}$ is the pure compound solubility of component i ($x_{i(w)}^0$). A more detailed examination of thermodynamic principles involved in the two-phase hydrocarbon-water system is presented in a later section.

Leinonen and Mackay (1973) equilibrated hydrocarbon-water systems by agitation followed by settling. They admitted difficulties in removing resulting droplets and discarded data that appeared to be at error due to droplets. Their analytical procedure involved a single solvent extraction with a higher molecular weight solvent, heptane, and analysis by gas chromatography. They examined the possible sources of experimental error and concluded: "In view of the very dilute solutions encountered it is difficult to obtain good accuracy with the extraction analytical procedure." (page 231). Leinonen and Mackay (1973) did not take into account the precision of their solubility measurements (i.e., they did not report or consider standard deviations or confidence

limits of the solubility values). Most of the experimental results, even as means of experimental determinations, were not given.

Some of the hydrocarbon mixture $\gamma_{i(h)}$ values were obtained by Leinonen and Mackay (1973) from published vapor-liquid equilibria (VLE) data. Other hydrocarbon mixture $\gamma_{i(h)}$ values used were estimated from published VLE data on similar systems. Errors associated with the $\gamma_{i(h)}$ values used by Leinonen and Mackay (1973) are not known.

Leinonen and Mackay (1973) analyzed the results of their data using unorthodox and improper statistics. They report their results as the "average deviation of experimental points (%)" from ideality and "average deviation due to $\gamma_{i(h)}$ (%)" for solubility measurements for a number of mixture compositions for each binary hydrocarbon pair as opposed to giving their experimental data. The precision of experimental values and their acknowledgement of the difficulties in obtaining good accuracy were not taken into account in the analysis of the data. They concluded: "The mixtures exhibit a positive deviation in solubility which can be attributed partly to the activity coefficients in the hydrocarbon phase being slightly greater than unity, however, there is also an additional enhancement in the solubility due to the reduction of the activity coefficient of the hydrocarbon in the aqueous phase." (page 233). This definite conclusion is not warranted because of the magnitude of probable experimental errors associated with the solubility data, possible errors associated with the $\gamma_{i(h)}$ values used and the improper statistical analysis of the data. The results of their study did, however, generally conform to the following equation describing the aqueous solubility of component i

resulting from a binary hydrocarbon mixture containing that component in contact with water:

$$x_{i(w)} = x_{i(h)} \gamma_{i(h)} x_{i(w)}^o \quad (2)$$

The aqueous solubility of more complex multicomponent hydrocarbon mixtures (3 or more components) was examined by Leinonen (1976). Oil phase activity coefficients were experimentally determined by gas chromatographic analysis of the vapor phase over the hydrocarbon mixture. Vapor phase analysis using a syringe sampling technique can have significant errors associated with incomplete sample transfer. The oil phase activity coefficient values for alkane mixtures determined by Leinonen (1976) were often significantly different from unity (e.g. 0.83, 0.85, 1.2, 4.1, 0.82, 1.4, 3.5, 3.5). These results vary significantly from those of Bronsted and Koefoed (1946) and Belnap and Weber (1961) who found alkane system activity coefficients to be close to unity, generally within 0.95 to 1.05. When the UNIFAC group-contribution method for estimating activity coefficients (Fredenslund et al., 1977) is used for these types of alkane systems, the activity coefficients calculated are also very close to unity. Hydrocarbon phase interactions in alkane systems are expected to be small due to the structural and chemical similarities of the compounds. Hydrocarbon phase activity coefficients such as 0.83 or 3.5 for mixtures of alkanes would indicate a significant error in their determination.

The basic conclusions of Leinonen (1976) agree with those of Leinonen and Mackay (1973) in that hydrocarbon solubility resulting from mixtures was enhanced by the presence of hydrocarbon co-solutes which cause a reduction in the hydrocarbon activity coefficient in the aqueous phase. Leinonen (1976) developed 'solubility enhancement

factors', e_i , to help predict the aqueous solubility of a given hydrocarbon i resulting from contact with a hydrocarbon mixture.

$$x_{i(w)} = x_{i(h)} x_{i(w)}^o e_i \quad (3)$$

The enhancement factor used varied with hydrocarbon type: 1.4 for alkanes, 1.4 for cycloalkanes, 2.2 for aromatics and 1.8 for olefins.

Leinonen (1976) used the enhancement factor approach to predict the solubilities of two gasolines and a crude oil with a maximum error of 7.5%. Errors in the solubility prediction of many of the individual components were, however, considerably greater than 7.5%. Leinonen derived his enhancement factors from a series of mixture solubilities. The mixture compositions containing aromatic components generally had a total aromatic mole fraction of approximately 0.2 with the remainder of the mixture comprised of aliphatics. This was probably chosen with the knowledge that crude oils and petroleum fuels often have a mole fraction of approximately 0.2 for the total aromatics in the mixture. Leinonen also stated that: "Although concentration affects the activity coefficients, it was not considered as a parameter and it varied from 0.5 mole fraction for some components to less than 0.01 mole fraction for others in the various solutions." (page 32). Concentration effects were definitely considered by Leinonen when selecting the compositions of the mixtures studied, thus biasing the enhancement factors in favor of a hydrocarbon mixture having a composition resembling that of petroleum and not of hydrocarbon mixtures, in general. The composition of a hydrocarbon mixture can greatly affect the hydrocarbon mixture activity coefficients. A mole fraction change for a component from 0.5 to 0.1 could change the oil phase activity coefficient from 1.3 to 2.0,

a difference that could cause a 35% difference in the predicted solubility if $\gamma_{i(h)}$ was used instead of e_i .

Leinonen (1976) apparently biased his experimental design to favor hydrocarbon mixtures of the general component type composition of a petroleum fuel as well as to favor the solubility prediction of the more soluble components (i.e. lower molecular weight aromatics) which might explain why the "enhancement factors" gave the appearance of working in the prediction of the gasoline and oil solubilities. Neither Leinonen and Mackay (1973) nor Leinonen (1976) proved that there was a significant reduction in the hydrocarbon activity coefficient in the aqueous phase. Both solubility and oil phase activity coefficient determinations may contain significant errors which were not taken into consideration.

The aqueous solubility of mixtures of solid hydrocarbons was examined by Eganhouse and Calder (1976) in an effort to elucidate the dissolution process of petroleum hydrocarbons. Mixtures of solid hydrocarbons were found to generally yield component concentrations in water that were the same as the pure compound solubility of that component. Some of the solid mixtures examined, however, yielded component solute concentrations considerably below their pure component solubility. Eganhouse and Calder stated that "it is clear that solute-solute interaction and/or the formation of solid solutions are influencing the aqueous solubility of these medium molecular weight aromatic hydrocarbons." (page 558). Eganhouse and Calder failed to examine the phase behavior of the solid mixtures in question, which may have at least partially explained the reduced solubilities. The results of Eganhouse and Calder (1976) add little to understanding of

the aqueous solubility of aromatic compounds present in petroleum and fuels, since these are liquid mixtures.

Green and Frank (1979) measured the aqueous solubilities of solutions of benzene in carbon tetrachloride and in cyclohexane. The benzene + cyclohexane mixtures are very similar to several of the mixtures examined by Leinonen and Mackay (1973) (e.g. benzene + n-hexane and benzene + 2-methylpentane). Green and Frank were primarily concerned with determining if Henry's Law coefficient values differed significantly from constancy. They were also concerned about the possible solute dimerization of benzene suggested by Reid et al. (1969) and the possible 'hydrophobic-bond-forming tendency' of benzene in water suggested by Ben-Naim et al. (1973). Green and Frank observed no change in the Henry's Law coefficient values within the precision of water solubility measurements, thus they did not detect effects due to possible solute dimerization. The conclusion of Green and Frank's work in contrast to that of Leinonen and Mackay (1973) was that the hydrocarbon phase activity coefficients explained essentially all of the enhanced solubility beyond ideal solubility (i.e. eq. 2 with $\gamma_{i(h)}$ assumed to be unity) and there was no significant reduction in the hydrocarbon activity coefficient in the aqueous phase.

Tewari et al. (1982) examined the aqueous solubility of some binary liquid mixtures of organic compounds. They stated that single component systems have been examined in detail but "similar investigations have not been conducted on multicomponent organic systems despite their thermodynamic interest and environmental significance." (page 436). A satisfactory review of the literature was clearly not undertaken since Leinonen and Mackay (1973), Leinonen

(1976) and Green and Frank (1979) all investigated the aqueous solubility of liquid multicomponent organic systems. Tewari et al. (1982) chose to use volume fractions instead of mole fractions in equation (2). Volume fractions are more difficult to use since excess volumes of mixing may have to be taken into account for some mixtures and such data are difficult to obtain. The results of Tewari et al. (1982) basically agree with those of Green and Frank (1979) in that the enhanced solubility above the ideal solubility can be accounted for by the organic activity coefficient in the organic phase.

The solubility of organic mixtures (liquid, solid or mixed) was examined by Banerjee (1984). The UNIFAC group-contribution method was used to predict organic phase activity coefficients. Equation (2) was found to adequately predict solute concentrations resulting from liquid mixtures. Component activity coefficients in the aqueous phase were not observed to be affected by the presence of cosolutes (i.e. no reduction in the aqueous phase activity coefficient was detected). The use of UNIFAC, however, is adequate only as a first approximation. UNIFAC calculated activity coefficients may agree very well with experimentally determined activity coefficients in some mixtures but not so well in others. The work of Banerjee (1984) is not a rigorous thermodynamic investigation of the aqueous solubility of liquid organic mixtures.

Large biomolecules have specific configuration(s) in aqueous media which are required for the appropriate biochemical processes to occur. The active configuration can be lost and the biochemical processes halted if the solvent (water) is altered by the addition of alcohol. The importance of the solvent water in biochemical processes

such as enzymatic reactions and membrane formation is evident. Phenomena concerning the role of water in these processes have been termed 'hydrophobic interactions' (see Tanford, 1980; and Ben-Naim, 1980). Hydrophobic interactions are not well understood and have been the subject of much research and speculation over the past 15 years. The term 'hydrophobic interactions' has been loosely used to include the solubility properties of hydrophobic molecules in water and solute-solute interactions of apolar species in water. The latter may be more correctly thought of as "solvent-induced interactions between apolar species in water" (Pratt and Chandler, 1980; page 2). Two apolar molecules or parts of a large biomolecule which are sufficiently close to each other in aqueous solution may be forced to proximity or contact by the water molecules through changing structure in vicinity of the apolar species. This minimizes the amount of structured water required in the hydration spheres, an entropically favorable occurrence. It must be stressed that these effects of changing water structure are theoretical and their existence is under debate. The only experimental evidence possibly detecting solvent-induced apolar solute interactions is that of Tucker et al. (1981) who made precise determinations of Henry's Law coefficient values (K_H) for benzene at different concentrations and observed a decrease in K_H as the aqueous phase concentration increased. The decrease in K_H was interpreted as the result of the formation of 'dimers' of benzene (i.e. solvent-induced solute interactions). If this interpretation is correct, approximately 3-4% of the benzene in solution at saturation is in 'dimers'. This observation is important because it gives a possible indication of the magnitude of effect supposedly caused by the solvent-induced solute

interactions form of hydrophobic interactions for hydrocarbons in water. This type of hydrophobic interaction is a possible explanation for the apparent reduction in aqueous phase activity coefficients observed by Leinonen and Mackay (1973) and Leinonen (1976). The possible magnitude of the effect of such interactions for benzene (Tucker et al., 1981) indicates, however, that a reduction in aqueous phase activity coefficients for a hydrocarbon mixture would not be detectable within the precision of water solubility determinations.

It should be noted that there is a lack of consistency in the use of the term 'hydrophobic interactions' in the literature. It is advisable not to use the term 'hydrophobic interactions' but rather 'aqueous phase solute-solute interactions' when discussing solvent-induced hydrophobic interactions.

Electrolyte solutions 'salt out' non-electrolyte solutes resulting in equilibrium concentrations for the non-electrolyte solutes lower than those found in distilled water (e.g., Gordon and Thorne, 1967; Sutton and Calder, 1975; Eganhouse and Calder, 1976; Whitehouse, 1984). Whitehouse (1984) also observed 'salting in' for 1,2-benzanthracene below 25°C. The effect of dissolved salts on the aqueous solubility of liquid hydrocarbon mixtures has not, as yet, been reported.

The 'solubilization' or 'accommodation' of hydrocarbons by the dissolved organic material (DOM) in seawater was examined by Boehm and Quinn (1973), who defined solubilized material as that which passes through a 0.5 μm filter and is not necessarily in true solution. The Boehm and Quinn study was primarily kinetic in nature. Results indicated that aliphatic hydrocarbons were solubilized more when DOM was present than when the DOM was removed from the seawater used in the

experiments. Aromatics appeared to be unaffected by the DOM. It is difficult to determine the meaning and significance of the work of Boehm and Quinn since the results were highly dependent upon the particular experimental design used and neither steady state nor equilibrium conditions existed.

Hashimoto et al. (1984) examined the solubility of various aromatic hydrocarbons in seawater and artificial seawater, and concluded that the DOM in seawater had an insignificant effect on the solubility of the compounds tested.

Using a dynamic coupled column liquid chromatographic technique, Whitehouse (1985) examined the effects of DOM on the aqueous 'partitioning' of polynuclear aromatic hydrocarbons (PAH). In most cases aqueous partitioning was simply the compound's aqueous solubility because the solute concentration with DOM was usually the same as without. The main cases in which DOM increased the amount of PAH solubilized were those in which fairly high concentrations of DOM of terrestrial origin was used with very low solubility PAH's. The experimental design of Whitehouse (1985) has definite advantages over that of Boehm and Quinn (1973) since steady state, if not equilibrium, conditions existed.

The composition of a reservoired petroleum may change due to water washing which removes the more soluble components of the oil (Bailey et al., 1973). Water washing in combination with other processes such as inorganic oxidation and biodegradation may significantly alter reservoired oils in mature basins so that the influence of the original source is obscured. Water washing may occur concurrently with petroleum migration. The problems associated with current

understanding, conjectures and beliefs regarding the process(es) of petroleum migration are outlined by Roberts and Cordell (1980). The one point that most authors on the subject of petroleum migration agree upon is that migration must have occurred (i.e. the hydrocarbons found in a reservoir rock did not originate there). Beyond this common agreement, however, lie numerous areas involving substantial differences of opinion. As to the role of water: "There are those who think that water has very little to do with the transfer of organic material from source to trap, and there are those who think that water is almost totally responsible for the transfer." (Roberts and Cordell, 1980; page vii). The 'problem' of petroleum migration is poorly formulated and unsolved, but it appears that an improved understanding of the aqueous solution behavior of liquid hydrocarbon mixtures may be helpful.

THERMODYNAMIC INVESTIGATIONS

1. Thermodynamic Principles

A thermodynamic system of a hydrocarbon in its pure state in contact with water yields the following equations for chemical potential (μ):

$$\mu_{i(h)}^o = \mu_i^* + RT \ln \gamma_{i(h)}^o x_{i(h)}^o \quad (4)$$

$$\mu_{i(w)}^o = \mu_i^* + RT \ln \gamma_{i(w)}^o x_{i(w)}^o \quad (5)$$

,where γ and x are the activity coefficient and mole fraction, respectively. The superscripts o and $*$ denote a single hydrocarbon in the hydrocarbon phase and the standard state for the pure hydrocarbon, respectively. Subscripts i , (h) and (w) denote the i^{th} component, hydrocarbon phase and aqueous phase, respectively.

Equilibration is achieved when $\mu_{i(h)}^o = \mu_{i(w)}^o$, thus:

$$x_{i(w)}^o = x_{i(h)}^o \frac{\gamma_{i(h)}^o}{\gamma_{i(w)}^o} \quad (6)$$

A thermodynamic system of a multicomponent hydrocarbon mixture in contact with water yields the following equations for chemical potential:

$$\mu_{i(h)} = \mu_i^* + RT \ln \gamma_{i(h)} x_{i(h)} \quad (7)$$

$$\mu_{i(w)} = \mu_i^* + RT \ln \gamma_{i(w)} x_{i(w)} \quad (8)$$

Equilibrium is achieved when $\mu_{i(h)} = \mu_{i(w)}$, thus:

$$x_{i(w)} = x_{i(h)} \frac{\gamma_{i(h)}}{\gamma_{i(w)}} \quad (9)$$

Dividing eq.(9) by eq.(6), we obtain:

$$x_{i(w)} = \frac{x_{i(h)} \gamma_{i(h)} \gamma_{i(w)}^o}{x_{i(h)}^o \gamma_{i(h)}^o \gamma_{i(w)}} x_{i(w)}^o \quad (10)$$

This is the basic equation for equilibrium dissolution of hydrocarbons in water. Assuming a negligible amount of water is present in the hydrocarbon phase (e.g., 0.00006 mole fraction H_2O in n-octane at $20^\circ C$, Englin et al., 1965), both $x_{i(h)}^O$ and $\gamma_{i(h)}^O$ are unity. This is generally believed to be valid, but a significant amount of water may be present in the hydrocarbon phase at higher temperatures. If the aqueous solubility of hydrocarbon i is not significantly affected by the presence of other hydrocarbons in the aqueous phase (i.e. via hydrophobic interactions or some other phenomena), then $\gamma_{i(w)}^O$ equals $\gamma_{i(w)}$ and eq.(10) reduces to eq.(2):

$$x_{i(w)} = x_{i(h)} \gamma_{i(h)} x_{i(w)}^O \quad (2)$$

Depending upon the particular hydrocarbons in the multicomponent mixture, there may be significant interaction in the hydrocarbon phase. The definition of ideal solution behavior follows if there are no interactions in the hydrocarbon phase.

$$x_{i(w)} = x_{i(h)} x_{i(w)}^O \quad (11)$$

The question central to this study is whether or not the presence of other hydrocarbons in the aqueous phase can significantly affect the solubility of a given hydrocarbon i (i.e. Does $\gamma_{i(w)}^O$ essentially equal $\gamma_{i(w)}$?). The most direct approach to this question is to determine $\gamma_{i(h)}$ values by a method independent of solubility measurements. Comparison of independently determined $\gamma_{i(h)}$ values with $\gamma_{i(h)}$ values calculated using solubility measurements and eq. (2) can determine if $\gamma_{i(w)}$ is not significantly different from $\gamma_{i(w)}^O$ if the $\gamma_{i(h)}$ values determined by the two methods do not differ significantly.

Component activity coefficients in the hydrocarbon mixture hydrocarbon phase can be determined by examining the vapor phase above

the mixture for deviations from Raoult's law. Raoult's law assumes ideal behavior in the liquid or organic phase.

$$p_i = x_{i(h)} p_i^{\circ} \quad (12)$$

, where p_i is the partial pressure of component i and p_i° is the pure component i vapor pressure. If significant component interactions exist in the liquid hydrocarbon phase, $\gamma_{i(h)}$ can be calculated from the deviation from Raoult's law.

$$p_i = \gamma_{i(h)} x_{i(h)} p_i^{\circ} \quad (13)$$

Vapor-liquid equilibria data can be used to experimentally determine $\gamma_{i(h)}$ values. Partial vapor pressure measurements are generally very difficult to determine with accuracy. Total vapor pressure measurements can, however, generally be determined with considerable accuracy if at least one of the components is sufficiently volatile. The total vapor pressure (P) is the sum of the partial vapor pressures. For a binary mixture of A and B:

$$P = \gamma_A x_A p_A^{\circ} + \gamma_B x_B p_B^{\circ} \quad (14)$$

Various empirical equations exist which can be used to describe the activity coefficients as a function of composition (e.g. van Laar equations, Margules equations, Redlich-Kister equations, Wohl equations). The empirical equation used must be consistent with the Gibbs-Duhem equation:

$$\sum x_i d\mu_i = 0 \big]_{T,P} \quad (15)$$

The chemical potentials are related to activity coefficients, thus the Gibbs-Duhem equation can be written for a binary mixture of A and B as:

$$x_A d\ln \gamma_A + x_B d\ln \gamma_B = 0 \big]_{T,P} \quad (16)$$

At low pressures, the pressure dependence of the activity coefficients can be neglected. The following general expression is a form of the Gibbs-Duhem equation relating a partial molar quantity (\bar{q}_i) to the total molar quantity (Q):

$$\bar{q}_i = Q + (1-x_i) \left[-\frac{Q}{x_i} \right]_{T,P} \quad (17)$$

Excess thermodynamic functions of mixing can be calculated from the activity coefficients. The molar excess free energy of mixing (G^E) can be calculated from:

$$G^E = - \sum x_i RT \ln \gamma_i \quad (18)$$

G^E for a binary system as a function of composition can be represented by the infinite series:

$$G^E = x_A x_B (B' + C'(x_A - x_B) + D'(x_A - x_B)^2 + \dots) \quad (19)$$

Expressions consistent with the Gibbs-Duhem equation relating activity coefficients for a binary system to G^E are:

$$RT \ln \gamma_A = G^E + x_B \left[-\frac{G^E}{x_A} \right]_{T,P} \quad (20)$$

and

$$RT \ln \gamma_B = G^E - x_A \left[-\frac{G^E}{x_A} \right]_{T,P} \quad (21)$$

Combining equations (19) with equations (20) and (21) yields the Redlich-Kister equations (Redlich et al., 1952) for binary mixture activity coefficients:

$$\begin{aligned} \log \gamma_A &= x_B^2 (B + C(3x_A - x_B) + D(x_A - x_B)(5x_A - x_B) \\ &\quad + E(x_A - x_B)^2(7x_A - x_B) + \dots) \quad (22) \\ \log \gamma_B &= x_A^2 (B - C(3x_B - x_A) + D(x_B - x_A)(5x_B - x_A) \\ &\quad - E(x_B - x_A)^2(7x_B - x_A) + \dots) \end{aligned}$$

In most cases, the expansion can be truncated at three terms and remain sufficiently accurate. The problem then becomes one of determining the coefficients B, C and D. A commonly used method of determining the Redlich-Kister coefficients from total vapor pressure measurements is that of Barker (1953)(King, 1969, pages 346-349, gives a description of this method for the Redlich-Kister equations). The method determines values of B, C and D such to minimize the root mean square deviations between the observed and calculated vapor pressures by use of the method of least squares.

The standard state free energy change ($\Delta G_{i,s}^{\circ}$) for the solution process can be expressed as:

$$\Delta G_{i,s}^{\circ} = -RT \ln x_{i(w)}^{\circ} \quad (23)$$

The standard state enthalpy change for the solution process can be calculated using the Gibbs-Helmholtz equation.

$$\left(\frac{\Delta G_{i,s}^{\circ}}{T} \right)_P = - \frac{\Delta H_{i,s}^{\circ}}{T^2} \quad (24)$$

The standard state entropy change for the solution process can then be calculated using:

$$\Delta G_{i,s}^{\circ} = \Delta H_{i,s}^{\circ} - T \Delta S_{i,s}^{\circ} \quad (25)$$

2. Vapor Pressure Experiments

a. Materials and Methods

The design of the vapor pressure apparatus used in the 20.0°C experiments is shown in Figure 1. The hydrocarbon mixtures or pure components were added to the vessel by disconnecting the Cajon fitting at the top of the vessel. The water bath was temperature controlled to 20.00 ± 0.03°C. Water temperature was monitored using a Parr

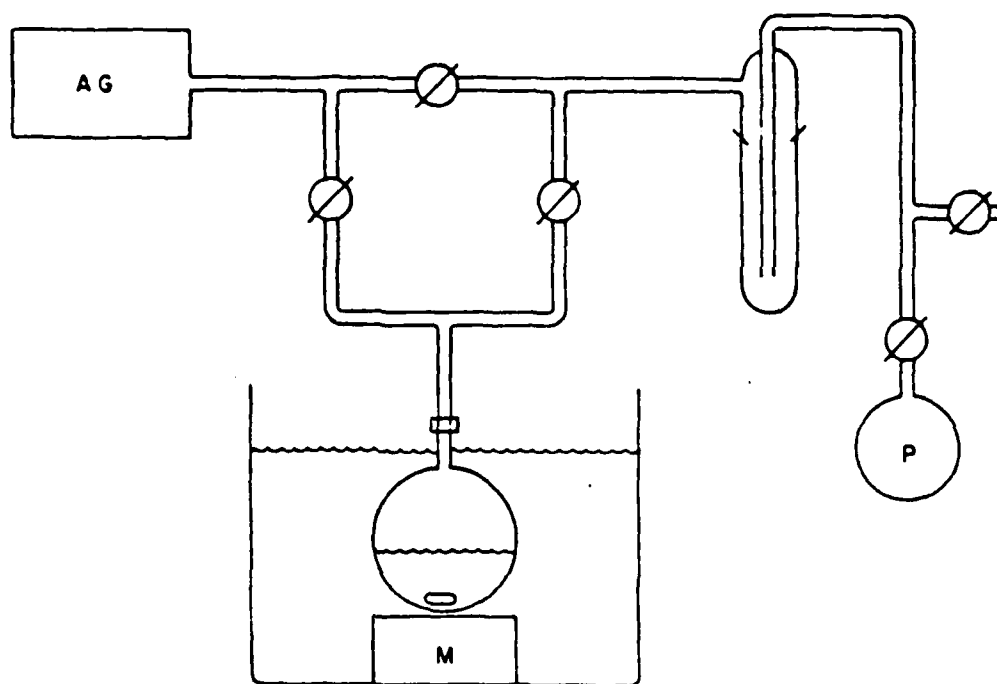


Figure 1 . Schematic of vapor pressure apparatus used in 20°C experiments. AG - absolute gauge; M - magnetic stirrer; P - pump.

Instrument Co. mercury thermometer ($19 - 25^{\circ}\text{C}$ with 0.01°C divisions). The mercury thermometer was calibrated against a platinum resistance thermometer described below. The vacuum trap was placed in liquid nitrogen to prevent pump oil contamination. The vacuum stopcocks were opened to allow for pump-down and degassing. A pump-down time of 6 minutes was determined to be adequate, except for pure 1-methylnaphthalene and pure tetralin, which required more time. Two of the three stopcocks were then closed to allow the system from the vessel to the pressure gauge to be open. The vapor pressure was determined with a Datametrics Barocel Type 600A ($0.01 - 100.0$ torr range) pressure sensor coupled with a Datametrics Type 1500 pressure readout unit. This unit was new and calibrated by Datametrics.

Mixture compositions changed as a result of the pump-down process. Samples were removed immediately following vapor pressure measurement and mixture compositions were determined by refractometry using a Bausch and Lomb Refractometer (Abbe 3-L). Refractive index calibrations for the binary mixtures examined are given in Table I. The higher purity methylcyclohexane and ethylbenzene were used in the vapor pressure experiments, as well as in the corresponding water solubility experiments.

The design of the vapor pressure apparatus used in the 70.0°C experiment is shown in Figure 2. The hydrocarbon mixtures or pure components were added to the vessel through the septum cap opening (cap removed) with the water bath level lowered. The level was then raised and water temperature was maintained at $70.00 \pm 0.03^{\circ}\text{C}$ for the time in which the vapor pressure reading was taken. The water bath temperature was measured by a platinum resistance thermometer (Weed Instrument Co.,

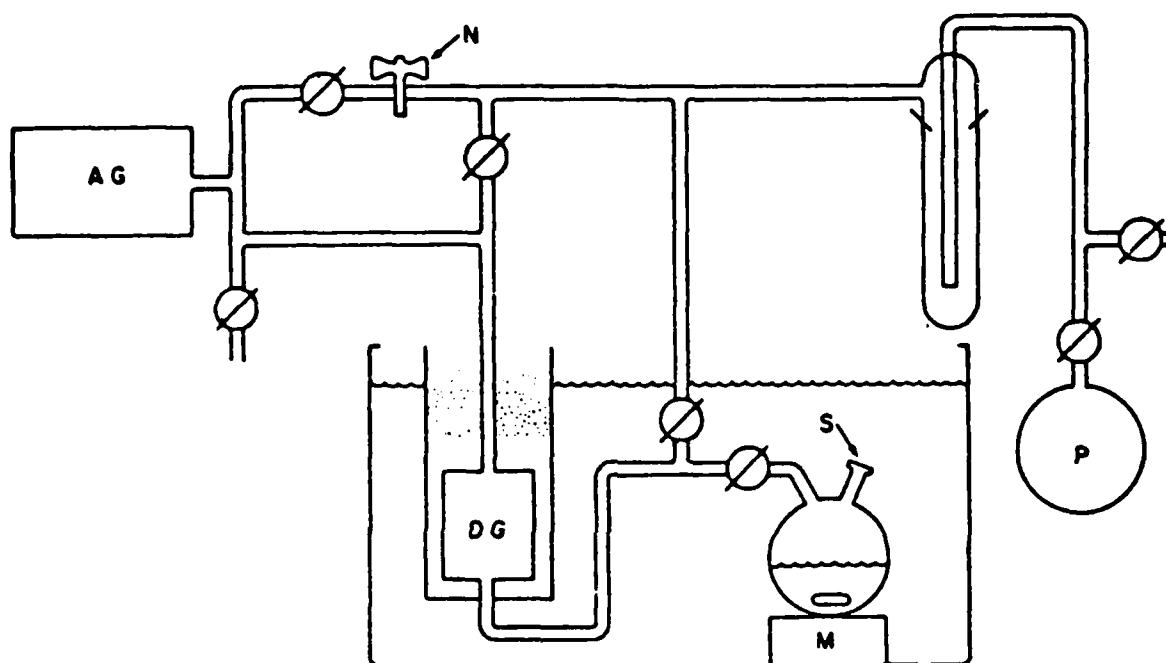


Figure 2. Schematic of vapor pressure apparatus used in 70°C experiment. AG - absolute gauge; DG - differential gauge; M - magnetic stirrer; S - septum; P - pump.

TABLE I. Binary hydrocarbon mixture refractive index calibrations at 21°C.

<u>Mole Fraction A</u>	<u>Refractive Index</u>	<u>Mole Fraction A</u>	<u>Refractive Index</u>
<u>n-octane (A) + 1-methylnaphthalene</u>		<u>tetralin (A) + methylcyclohexane</u>	
1.0000	1.3973	1.0000	1.5407
0.8958	1.4173	0.8966	1.5293
0.7963	1.4368	0.7940	1.5181
0.7000	1.4565	0.6954	1.5068
0.5920	1.4798	0.5962	1.4955
0.5022	1.4985	0.4984	1.4839
0.3994	1.5210	0.4088	1.4732
0.2922	1.5452	0.2942	1.4593
0.1972	1.5671	0.1998	1.4477
0.1005	1.5904	0.1011	1.4354
0.0000	1.6146	0.0000	1.4227
<u>ethylbenzene (A) + n-octane</u>			
1.0000	1.4948		
0.9031	1.4821		
0.8006	1.4696		
0.6931	1.4574		
0.5918	1.4469		
0.5014	1.4380		
0.4051	1.4290		
0.3063	1.4204		
0.2016	1.4119		
0.1024	1.4043		
0.0000	1.3971		

Model 101) with a Leeds and Northrup Type 8079 ER thermometer bridge and a Leeds and Northrup Type 9828 D.C. null detector. The vacuum trap was placed in liquid nitrogen. The vessel was pumped down and degassed by opening the two vacuum stopcocks in the water bath. A pump-down time of 4 minutes was determined to be adequate for degassing, except for pure 1-methylnaphthalene. The immersed stopcock closest to the pump was then closed to allow the system to be open from the vessel to the differential gauge (Datametrics Barocel Type 536 pressure sensor, 0.001 - 10 torr range, coupled with a Datametrics Barocel Electronic Manometer Type 1174 readout unit). The pressure on the opposite side of the differential gauge was adjusted through the use of the four valves (one of which was a needle valve to regulate flow towards the pump) near the absolute pressure gauge (Datametrics Barocel Type 600A pressure sensor, 0.1 - 1000 torr range, coupled with the Datametrics Type 1500 pressure readout unit, the pressure sensor was new and calibrated by Datametrics) to give a null reading on the differential gauge. The absolute pressure gauge reading was then equal to the system pressure between the vessel and the differential gauge and was recorded. The water bath level was lowered and a hydrocarbon mixture sample was taken and analyzed by refractometry.

b. Results

The results of the vapor pressure experiments and the Redlich-Kister coefficients calculated using the method of Barker (1953) are given in Table II. An accuracy to the second decimal place in the vapor pressure determined $\gamma_{i(h)}$ values is required for the purpose of comparison with the water solubility determined $\gamma_{i(h)}$ values. It was

TABLE II. Hydrocarbon mixture vapor pressure results and Redlich-Kister coefficients calculated by the method of Barker (1953).

<u>Refractive Index</u>	<u>Mole Fraction A</u>	<u>Pressure (torr)</u>	<u>Redlich-Kister Coefficients</u>
n-octane (A) + 1-methylnaphthalene (1 st run at 20.0°C)			
-	1.000	10.39	B = 0.4764
1.4146	0.908	9.54	C = -0.008829
1.4335	0.812	8.79	D = 0.01153
1.4491	0.733	8.27	
1.4617	0.675	7.88	
1.4838	0.570	7.24	
1.4951	0.518	6.92	
1.5257	0.375	5.97	
1.5515	0.263	4.98	
1.5680	0.195	4.13	
1.5918	0.092	2.44	
-	0.000	0.03	
n-octane (A) + 1-methylnaphthalene (2 nd run at 20.0°C)			
-	1.000	10.35	B = 0.4732
1.4087	0.936	9.79	C = -0.01317
1.4177	0.891	9.39	D = 0.01513
1.4302	0.829	8.88	
1.4587	0.689	7.93	
1.4892	0.547	7.01	
1.5137	0.432	6.32	
1.5389	0.318	5.46	
1.5510	0.266	4.99	
1.5778	0.153	3.46	
1.5910	0.093	2.47	
-	0.000	0.03	
n-octane (A) + 1-methylnaphthalene (70.0°C)			
-	1.000	118.4	B = 0.4104
1.4197	0.880	106.5	C = -0.01988
1.4409	0.776	96.8	D = 0.02329
1.4632	0.670	88.3	
1.4752	0.612	83.9	
1.4967	0.509	75.8	
1.5110	0.444	70.3	
1.5324	0.348	61.9	
1.5597	0.229	48.3	
1.5954	0.078	28.0	
-	0.000	1.4	

TABLE II. Continued.

<u>Refractive Index</u>	<u>Mole Fraction A</u>	<u>Pressure (torr)</u>	<u>Redlich-Kister Coefficients</u>
<u>tetralin (A) + methylcyclohexane (20.0°C)</u>			
-	1.000	0.15	B = 0.2106
1.5301	0.904	5.13	C = -0.01278
1.5194	0.805	9.63	D = 0.01742
1.5096	0.720	13.11	
1.4958	0.599	17.43	
1.4878	0.531	19.60	
1.4791	0.458	21.98	
1.4696	0.379	24.31	
1.4574	0.279	27.38	
1.4447	0.176	30.44	
1.4296	0.055	34.37	
-	0.000	36.14	
<u>ethylbenzene (A) + n-octane (20.0°C)</u>			
-	1.000	7.08	B = 0.2029
1.4780	0.872	8.18	C = 0.05873
1.4684	0.792	8.74	D = -0.005218
1.4579	0.698	9.26	
1.4491	0.614	9.39	
1.4368	0.487	9.74	
1.4282	0.397	9.92	
1.4175	0.275	10.13	
1.4108	0.200	10.24	
1.4043	0.105	10.32	
-	0.000	10.36	

important to assess the affect of imperfections in the vapor phase on the resulting $\gamma_{i(h)}$ values since second virial coefficients at 20 and 70°C for the compounds of interest were not available. Jain et al. (1973) used total vapor pressure measurements and the method of Barker (1953) taking into account vapor phase imperfections (i.e., second virial coefficients) to determine $\gamma_{i(h)}$ values for an n-octane + benzene system at 25 and 55°C. If the vapor phase imperfections are not accounted for, the same activity coefficients are calculated to the second decimal place. The n-octane + benzene system is similar to the systems examined in these experiments, thus it can be assumed with reasonable certainty that vapor phase imperfections make a sufficiently minor contribution to the calculated $\gamma_{i(h)}$ values to be disregarded.

The single compound vapor pressures are in good agreement (generally within 2%) of API Project 44 vapor pressures.

3. Water Solubility Determinations

The accuracy and/or precision of solubility determinations are important criteria to take into account when drawing conclusions based upon solubility data. It is difficult to describe the closeness of an experimental measurement to the 'true' value. The best that can be hoped for is a reasonable amount of confidence in the accuracy of the experimental results. The low solubility of the compounds used in this study makes solvent extraction followed by chromatographic analysis the preferred method for routine analysis of the solubility of hydrocarbon mixtures. Errors due to chromatography can be reduced by use of internal standard quantification. The primary drawback of the solvent extraction method is that the efficiency of the extraction procedure is

generally not well known. Accordingly, the solubility of 1-methylnaphthalene was also determined by a procedure using radiolabelled 1-methylnaphthalene and liquid scintillation counting which did not involve solvent extraction. The use of a radiolabelled compound has the drawback that the solubility value determined may be high due to the possible presence of radiolabelled polar impurities. Comparison of solubility values determined by the two methods gives an indication of the minimum extraction efficiency.

Comparison of experimental solubility values with solubility values in the literature can add a degree of confidence if good agreement is found, but may only indicate the presence of gross errors. Solubilities of pure hydrocarbons determined within this study were therefore compared with literature values.

For some aspects of this study, absolute accuracy is not as important as constancy of systematic errors (i.e. that the extraction efficiency of a given compound remain reasonably constant). This is of particular importance in the examination of deviations from ideal solution behavior (indicated by equation (2) when $\gamma_{i(h)}$ is unity). It is reasonable to expect that the systematic errors due to an extraction procedure would be constant if adequate precautions are taken and the procedure replicated.

Conclusions drawn from experimental data must be made taking the precision (random error) of the data into account. The precision is limited by the analytical procedure used, in this case gas chromatography with flame ionization detection, in conjunction with the reproducibility of all procedures prior to analysis. Inappropriate

conclusions can be made if the precision of the experimental data is not accounted for.

a. Materials and Methods

The hydrocarbons used are listed below by supplier. The stated purity or grade is given in parentheses. Aldrich Chemical: naphthalene (99+%); 1-methylnaphthalene (97% or 99%, only 97% purity was available at the beginning of the study); 1,4-dimethylnaphthalene (99%); 2-ethylnaphthalene (99+%); 1,2,3,4-tetrahydronaphthalene or tetralin (99%); ethylbenzene (99%); n-butylbenzene (99+%); n-octane (99+%); methylcyclohexane (99%); n-dodecane (99%); n-tridecane (99+%); n-pentadecane (98%). Pfaltz and Bauer: 1,3,5-triethylbenzene (99%). Eastman Kodak: ethylbenzene (98%); n-decane (98%); n-undecane (99%). Matheson, Coleman and Bell: n-tetradecane (99%). Lancaster Synthesis: methylcyclohexane (99.9%). Amersham: 1-(C¹⁴)methylnaphthalene (specially synthesized and prepared to be free of polar impurities by supplier). Burdick and Jackson: toluene (distilled in glass); n-pentane (distilled in glass). Note that two suppliers are listed for ethylbenzene and methylcyclohexane. Unless otherwise stated, the supplier with the less pure grade was used. All chemicals were used as received except for 1-methylnaphthalene (not radiolabelled) which was purified by elution through a column of activated silica gel to remove interfering polar impurities. Organic-free water was obtained from a Culligan Aqua-Cleer Reverse Osmosis System.

The design of the solubility vessels used in the solubility experiments below 30°C is shown in Figure 3. The vessel design used for experiments above 30°C is the same except that a Cajon o-ring seal

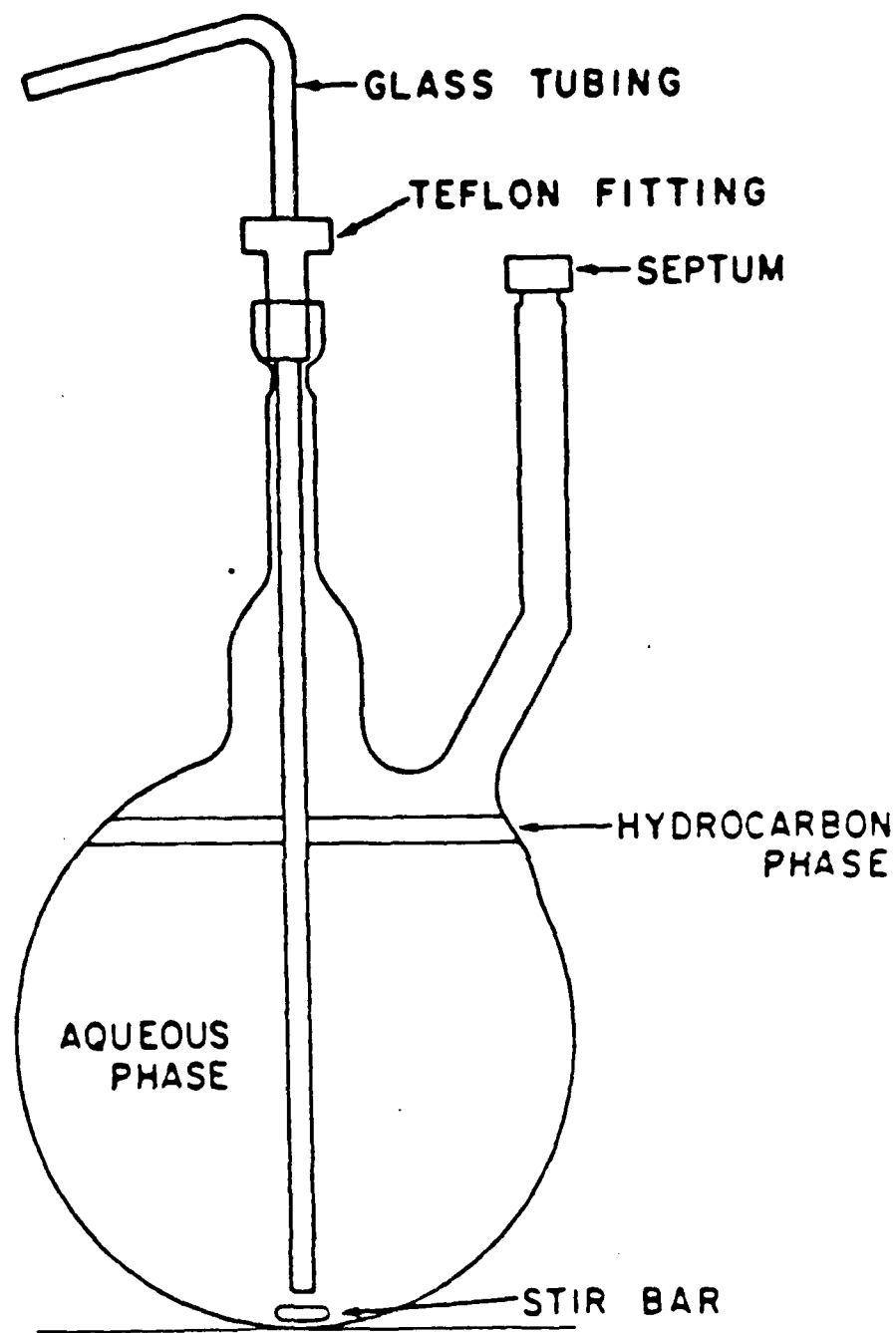


Figure 3. Design of water solubility vessel.

was used in place of the Teflon fitting and the tip of the glass tubing was drawn closed and broken prior to sampling.

The hydrocarbon phase was added to the vessel after addition of approximately 400 ml water. The amount of hydrocarbon phase added was selected so that the hydrocarbon phase composition did not change significantly (less than 1% per component) upon equilibration. The contents of the vessels were stirred without disturbance of the hydrocarbon-water interface for a minimum of 48 h. In initial experiments the vessels were also allowed to set undisturbed for 24 h prior to sampling. The setting period was later found to be unnecessary and was omitted. Laser light scattering observations indicated that droplets were not present. The temperature of the vessels was controlled by use of either incubators or water baths. The incubators were used initially but could only be controlled within 0.5 to 1.0°C. Water baths were usually controlled within 0.2°C, allowing the maximum possible temperature difference between runs to be 0.4°C. In the solubility experiments at temperatures over 30°C, the water level in the water bath had to cover the entire vessel, except the glass tubing, to prevent condensation from affecting the composition of the hydrocarbon phase.

Water samples were removed from the vessels by applying pressure through the septa with a syringe. Water samples were added directly to tared 60 ml separatory funnels which were reweighed to obtain the amount of water extracted (generally 20 - 25 ml). Two types of 60 ml separatory funnels were used: standard with ground glass stoppered tops and modified with the tops replaced with septum screw caps. The modified separatory funnels were used in the experiments examining

solubility as a function of temperature due to special sample handling precautions necessary to prevent vapor losses at higher temperatures. The samples were extracted by two different procedures depending upon the separatory funnel type used. **Standard separatory funnel:** Samples were extracted (for 2 minutes) with 1 ml pentane containing the appropriate internal standards. The pentane phase was isolated and the water extracted twice more with pentane (1 ml each). Pentane phases were combined then analyzed. **Modified separatory funnel:** Septum cap was screwed on immediately after sample was obtained. Samples were cooled in an ice water bath prior to addition of 1 ml neat pentane via a glass syringe through the septa. The sample was shaken for 1 minute then 1.00 ml pentane containing the appropriate internal standards was added and the funnel was shaken for 1 more minute. The pentane phase was isolated and the sample extracted twice more as before.

The use of internal standards was important for both accuracy and precision. Internal standards were: Methylcyclohexane was used initially for n-octane and vice versa. n-Nonane was later used for both n-octane and methylcyclohexane. 1,3,5-Triisopropylbenzene was used for all aromatics. In initial experiments, the internal standard solution was added in the separatory funnel to the first 1 ml of pentane using a 0.100 ml pipette. In later experiments, 1.00 ml of pentane already containing the internal standards was added to the separatory funnel for the first pentane extraction. The latter procedure was found to significantly increase precision. The volatility of pentane required special procedures to be followed in regard to the internal standard solutions. A significant amount of pentane evaporates from the volumetric flask over a period of two or

more days of use, thus altering the internal standard concentrations. To avoid this, a new internal standard solution had to be used for each day that extractions were done. Relative response factors were determined each day of gas chromatographic analysis by injecting a solution containing known amounts of internal standards and compounds of interest.

The gas chromatography conditions used were: Varian 2700 gas chromatograph modified for glass capillary columns, 20 m SE-52 glass capillary column, splitless injection at 240°C, flame ionization detector (FID) at 300°C, oven temperature programmed from 40 to 240°C at 10°C/min, helium carrier gas. FID response was integrated by a Hewlett-Packard Model 3354 Laboratory Data System.

When the incubators were used, three solubility vessels were equilibrated with a given mixture or pure component. Each vessel was analyzed twice to yield six values. When water baths were used, two solubility vessels were equilibrated with a given mixture or pure component. Each vessel was analyzed three times to yield six values. If a single value appeared to be at error, it was deleted if it failed the Q test at the 90% confidence level. It was rare that a value had to be deleted. A minimum of five values were used to calculate a mean and standard deviation for each concentration (e.g., for 1-methylnaphthalene: 30.6, 42.6, 31.2, 30.2, 30.3 and 31.1 mg/L. The 42.6 value can be deleted thus: $n=5$, $\bar{x}=30.7$, $SD=0.5$ and $\text{coef. of var.}=1.6\%$).

For the 1-(C¹⁴)methylnaphthalene solubility experiments, 1 millicurie of the labelled 1-methylnaphthalene was added to 25 ml of unlabelled 1-methylnaphthalene. This activity was calculated to yield sufficient activity in the water phase for efficient liquid

scintillation counting. After two vessels were equilibrated as above, 2.0 ml water samples were added to tared scintillation vials. Six samples were taken from each vessel. Vials were reweighed to obtain the weight of sample. 2.00 ml of methanol and 10.0 ml of Aquasol-2 scintillation cocktail (New England Nuclear) was added to each vial, and vials were shaken. Standards of the 1-(C¹⁴)methylnaphthalene spiked 1-methylnaphthalene encompassing the expected solubility were prepared in 50 ml volumetric flasks with methanol. For each standard, 2.00 ml standard solution, 2.00 ml H₂O and 10.0 ml Aquasol-2 was added to the scintillation vial. Blanks were also prepared using neat methanol and H₂O in the cocktail. Standards and blanks were done in duplicate. The scintillation vials were counted to 1.0% accuracy using a Beckman LS-150 Liquid Scintillation System.

b. Single Hydrocarbon Water Solubility Results

Hydrocarbon solubility data are shown in Table III. More solubility data are given for 1-methylnaphthalene and n-octane since binary mixtures containing these compounds were extensively studied in this investigation. When another person did the extractions, the pure compound solubilities needed were repeated to account for possible procedural bias. In general, replicate values were quite close to each other. Extrapolated 25°C solubility values presented for 1-methylnaphthalene and n-octane were obtained from an experiment examining solubility as a function of temperature which will be presented later. The standard curve used to determine 1-methylnaphthalene solubility in the radiolabelled solubility experiment is shown in Figure 4.

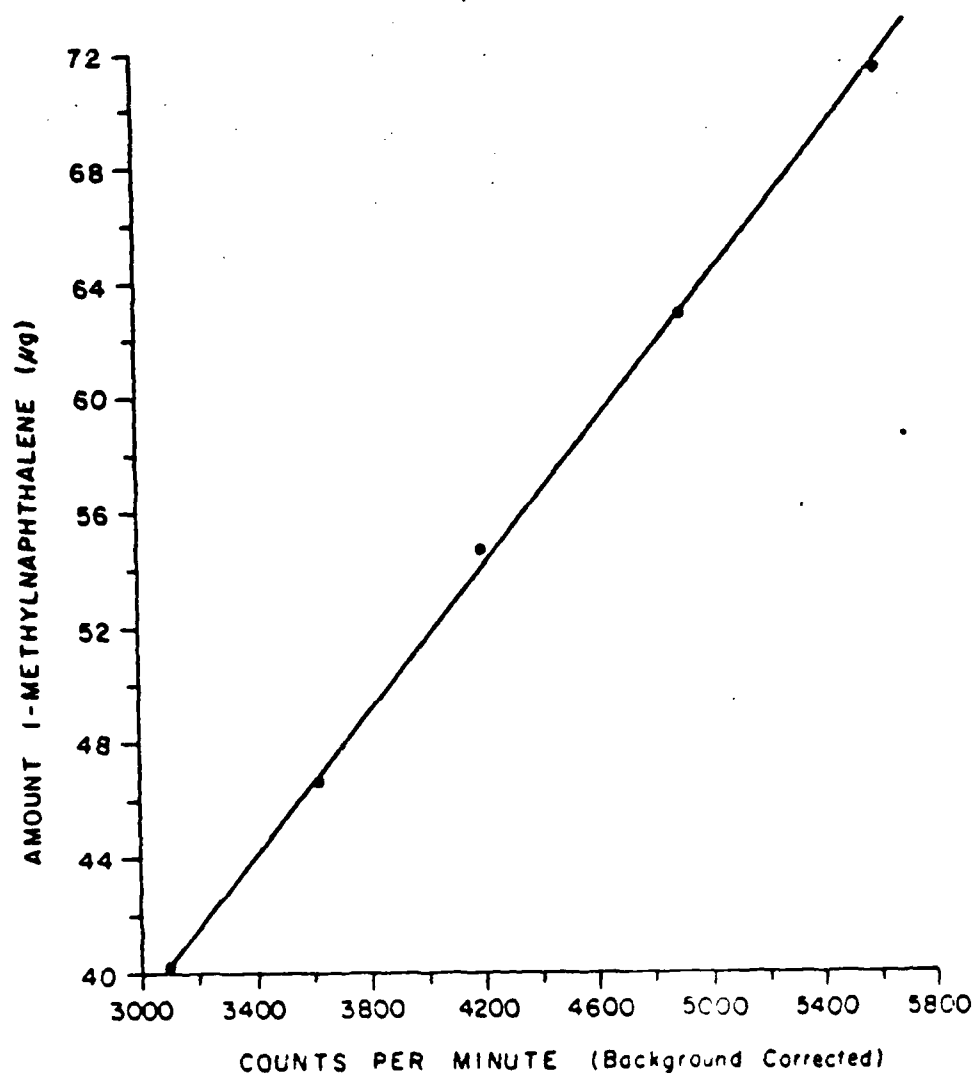


Figure 4. Standard curve used to determine 1-methylnaphthalene solubility in the radiolabelled water solubility experiment.

TABLE III. Hydrocarbon water solubilities (mg/L, $\bar{x} \pm 1$ SD) at 20°C (unless otherwise stated).

<u>Hydrocarbon</u>	<u>Solubility</u>	<u>Literature Solubility</u>	<u>Reference</u>
1-methylnaphthalene	30.5 \pm 0.2 ^a	25.3	9
	30.0 \pm 0.9 ^a	25.8 (25°C)	5
	29.6 \pm 0.3 ^a	28.5 (25°C)	8
	30.2 \pm 0.3		
	29.9 \pm 0.4		
	28.9 \pm 0.1 ^b		
	32.0 \pm 0.4 ^c		
	32.1 \pm 0.1 ^c		
	32.0 (25°C) ^{b, d}		
	89.8 \pm 0.3 (70°C) ^b		
	86.5 \pm 1.1 (70°C) ^b		
	89.4 \pm 1.2 (70°C) ^b		
	90.2 \pm 1.1 (70°C) ^b		
	87.9 \pm 1.5 (70°C) ^b		
n-octane	0.898 \pm 0.024 ^{a, e}	0.431 (25°C)	2
	0.890 \pm 0.031 ^a	0.66 (25°C)	1
	0.892 \pm 0.022 ^{a, e}	0.85 (25°C)	10
	0.837 \pm 0.019 ^{a, e}	0.88 (25°C)	11
	0.884 \pm 0.011		
	0.949 \pm 0.028		
	0.816 \pm 0.005 ^b		
	0.815 \pm 0.011 ^b		
	0.806 (25°C) ^{b, d}		
	1.79 \pm 0.02 (70°C) ^b		
	1.65 \pm 0.07 (70°C) ^b		
	1.73 \pm 0.06 (70°C) ^b		
	1.69 \pm 0.04 (70°C) ^b		
	1.46 \pm 0.03 (70°C) ^{b, g}		

TABLE III. Continued

<u>Hydrocarbon</u>	<u>Solubility</u>	<u>Literature Solubility</u>	<u>Reference</u>
naphthalene	25.3 \pm 0.5 ^a 27.0 \pm 0.3	31.3 (25°C) 33.6 (25°C) 31.2 (25°C)	5 6 7
2-ethylnaphthalene	9.47 \pm 0.39 9.21 \pm 0.09	8.00 (25°C)	5
1,4-dimethyl- naphthalene	9.55 \pm 0.21 ^a 9.91 \pm 0.20 ^a 9.47 \pm 0.14	11.4 (25°C)	8
1,2,3,4-tetrahydro- naphthalene	45.0 \pm 0.4 ^b 42.7 \pm 0.4 ^b		
methylcyclohexane	17.8 \pm 0.4 ^{a,f} 16.7 \pm 0.6 ^a 16.6 \pm 0.4 ^b 15.2 \pm 0.1 ^b	16.0 (25°C) 14.0 (25°C)	2 1
ethylbenzene	180 \pm 1 181 \pm 4	152 (25°C) 131 (25°C) 208 (25°C) 161 (25°C)	1 2 3 4
toluene	567 \pm 8	515 (25°C) 554 (25°C) 627 (25°C) 535 (25°C)	1 2 3 4
n-butylbenzene	13.3 \pm 0.2	11.8 (25°C)	4
n-hexylbenzene	0.889 \pm 0.017		
phenylcyclohexane	4.23 \pm 0.12		
1,2,3-triethyl- benzene	3.47 \pm 0.02		

TABLE III. Continued

- a - temperature control by incubator instead of water bath
- b - using modified separatory funnel extraction procedure
- c - solubility using 1-(C¹⁴)methylnaphthalene
- d - extrapolated value
- e - methylcyclohexane as internal standard instead of n-nonane
- f - n-octane as internal standard instead of n-nonane
- g - different n-nonane internal standard stock was used, which may account for lower value

References:

- 1 - McAuliffe, 1966
- 2 - Price, 1973
- 3 - Bohon and Claussen, 1951
- 4 - Sutton and Calder, 1975
- 5 - Eganhouse and Calder, 1976
- 6 - Gordon and Thorne, 1967
- 7 - Wauchope and Getzen, 1972
- 8 - Mackay and Shiu, 1977
- 9 - Schwarz, 1977
- 10- Polak and Lu, 1973
- 11- Nelson and Ligny, 1968

Literature values shown in Table III do not represent a complete search, but were located for the purpose of comparison. Although most of the literature values are for 25°C, they are still useful as a rough comparison.

The 1-methylnaphthalene solubility value using 1-(C¹⁴)methyl-naphthalene should be closest to the 'true' value, assuming that no radiolabelled polar impurities are present. As this assumption can not be tested with absolute certainty, it is assumed that the radiolabelled solubility value is at least a maximum value. The extraction procedure followed by gas chromatographic analysis, therefore, has at least a 93% efficiency (90% efficiency using the modified separatory funnel procedure).

c. Error Analysis and Discussion

There is fairly good agreement between solubilities determined in this study and those found in the literature. This agreement does not give any indication of accuracy, but it adds a degree of confidence to the data.

Solubility values were essentially the same, whether incubators or water baths were used for temperature control. The heat capacity of the water within the vessels may have allowed the vessel temperatures to remain near the middle of the temperature oscillation of the incubators.

All samples in which the modified separatory funnel extraction procedure was used gave slightly lower values than the initial extraction procedure, but the source of this difference is unknown.

Solubility values for 1-methylnaphthalene and n-octane at 70°C appear to be fairly reproducible. Some of the fluctuations in the values are believed to be caused by difficulties in controlling the water bath temperature.

Repeat analysis for a given compound using the initial extraction procedure, in general, gave reproducible results. This observation adds a measure of confidence to the procedure, and to its accuracy within a set of mixture solubility measurements.

Comparison of the radiolabelled solubilities with solvent extraction - gas chromatographic analysis solubilities for 1-methylnaphthalene indicate that the minimum extraction efficiency is about 90 to 93%. If a small amount of C¹⁴-labelled polar impurity raised the radiolabelled solubility slightly, the extraction efficiency would be greater. An extraction efficiency in this range is reasonable and it adds a degree of confidence to the solubilities determined by solvent extraction - gas chromatography.

Difficulties were encountered during analysis due to interfering peaks. Polar impurities in the 1-methylnaphthalene interfered with the integration of the 1-methylnaphthalene peak. Elution of the 1-methylnaphthalene through an activated silica gel column eliminated this problem. A small peak interfered with the integration on n-nonane. This problem was solved by altering the gas chromatograph's temperature program slightly. In one instance, a peak resulting from the 1-methylnaphthalene used interfered with n-octane. This problem was solved by obtaining a different lot of 1-methylnaphthalene from the supplier. Solubility values could have been altered 5 to 15% as a result of these interfering peaks. In some cases, the effect of a 5%

increase in a solubility value would have significantly changed the conclusions drawn from the data. Every effort was taken to detect possible interferences and to eliminate the effect they would have on the resulting solubilities. It is noted that most, if not all, of these interfering peak problems could have gone unnoticed if packed columns were used instead of glass capillary columns, because the interfering peak may not have been resolved from the peak of interest.

Absolute accuracy appears to be within approximately 10% of the values obtained based upon the radiolabelled 1-methylnaphthalene experiment. Relative accuracy was most likely quite good. Coefficients of variation were generally in the range of 0.5 to 3%. Considering that the FID response on repeat injections can yield a coefficient of variation of 0.5%, the remaining variations are caused by other factors such as reproducibility of extraction efficiency and errors caused by the analyst. A coefficient of variation in this range is considered good and would be difficult to reduce for a solvent extraction - gas chromatographic analysis procedure.

4. Water Solubility Experiments Corresponding to Vapor Pressure Experiments

The results of the water solubility experiments which correspond with the above vapor pressure experiments are given in Table IV. Water baths were used for temperature control in these experiments.

Hydrocarbon phase activity coefficients were calculated from the water solubility data using equation (2). The error (standard deviation) in the values used in the calculations were propagated to yield confidence limits for the calculated activity coefficients.

TABLE IV. Hydrocarbon mixture water solubility results corresponding to mixtures in Table II.

Mixture	Mole Fraction A	Solubility (mg/L, $\bar{x} \pm SD$)	
		A	B
n-octane (A) +	1.0000	0.884 \pm 0.011	0
1-methyl-	0.8961	0.813 \pm 0.033	7.86 \pm 0.16
naphthalene	0.7960	0.736 \pm 0.014	12.7 \pm 0.2
(20 °C)	0.6966	0.670 \pm 0.014	16.0 \pm 0.2
	0.5037	0.592 \pm 0.014	20.8 \pm 0.4
	0.3037	0.433 \pm 0.010	24.5 \pm 0.4
	0.1856	0.345 \pm 0.010	27.0 \pm 0.3
	0.0990	0.224 \pm 0.004	28.1 \pm 0.4
	0.0000	0	30.2 \pm 0.3
n-octane (A) +	1.0000	1.65 \pm 0.07 ^a	0
1-methyl-	1.0000	1.69 \pm 0.04 ^b	0
naphthalene	1.0000	1.73 \pm 0.06 ^c	0
(70 °C)	1.0000	1.79 \pm 0.02 ^d	0
	1.0000	1.46 \pm 0.03 ^{e,f}	0
	0.8945	1.54 \pm 0.03 ^a	19.5 \pm 0.2 ^a
	0.7906	1.46 \pm 0.07 ^b	32.9 \pm 0.5 ^b
	0.6881	1.31 \pm 0.02 ^c	43.5 \pm 0.3 ^c
	0.5000	1.20 \pm 0.02 ^d	58.4 \pm 0.3 ^d
	0.2944	0.690 \pm 0.015 ^{e,f}	68.9 \pm 0.5 ^e
	0.2040	0.583 \pm 0.010 ^{e,f}	74.4 \pm 0.5 ^e
	0.1034	0.345 \pm 0.009 ^{e,f}	79.4 \pm 0.7 ^e
	0.0000	0	86.5 \pm 1.1 ^a
	0.0000	0	90.2 \pm 1.1 ^b
	0.0000	0	89.4 \pm 1.2 ^c
	0.0000	0	89.8 \pm 0.3 ^d
	0.0000	0	87.9 \pm 1.5 ^e
tetralin (A) +	1.0000	42.7 \pm 0.4	0
methylcyclo-	0.8976	39.0 \pm 0.2	2.26 \pm 0.03
hexane	0.8019	35.4 \pm 0.2	4.08 \pm 0.08
(20 °C)	0.6985	31.6 \pm 0.2	5.74 \pm 0.05
	0.5043	24.3 \pm 0.1	8.57 \pm 0.06
	0.2926	16.1 \pm 0.1	11.3 \pm 0.1
	0.2017	11.9 \pm 0.1	12.4 \pm 0.1
	0.0966	6.29 \pm 0.05	13.7 \pm 0.1
	0.0000	0	15.2 \pm 0.1

TABLE IV. Continued.

<u>Mixture</u>	<u>Mole Fraction A</u>	Solubility (mg/L, $\bar{x} \pm SD$)	
		<u>A</u>	<u>B</u>
ethylbenzene (A)	1.0000	181 \pm 4	0
+ n-octane	0.8979	163 \pm 5	0.155 \pm 0.007
(20°C)	0.8009	148 \pm 2	0.252 \pm 0.003
	0.6964	137 \pm 5	0.354 \pm 0.021
	0.5021	103 \pm 2	0.492 \pm 0.018
	0.3024	67.8 \pm 1.6	0.635 \pm 0.033
	0.2018	48.8 \pm 0.8	0.729 \pm 0.029
	0.1213	29.3 \pm 0.3	0.827 \pm 0.048
	0.0000	0	0.949 \pm 0.028

a-e - vessels were equilibrated in same water bath, and resulting values from each set were used to determine corresponding water solubility method activity coefficient values in Table V.

f - new n-nonane internal standard stock solution was used which may account for lower values, however, water solubility calculated activity coefficients are not affected.

These and their corresponding static vapor pressure calculated activity coefficients are given in Table V.

There is no significant difference between the $\gamma_{i(h)}$ values calculated by the two methods when the precision of the water solubility determinations is taken into account. This is true even for the 70°C experiments with 1-methylnaphthalene and n-octane mixtures.

The hydrocarbon phase in the 70°C water solubility experiments contained a considerable amount of water. Figure 5 shows the amount of water in 1-methylnaphthalene and n-octane as a function of temperature (based upon the work of Eglin et al., 1965 and Brady et al., 1982). UNIFAC was used to calculate hydrocarbon phase activity coefficients for a 1-methylnaphthalene + n-octane mixture (9:1 mole fraction ratio), with and without water present in the hydrocarbon phase at 70°C and 150°C. Figure 5 and the results of Brady et al. (1982) were used to estimate the water content in the hydrocarbon phase. The UNIFAC results are given in Table VI. The UNIFAC values indicate that, for this binary hydrocarbon mixture up to 150°C, the presence of water in the hydrocarbon phase does not significantly affect the hydrocarbon phase activity coefficients.

5. 1-Methylnaphthalene, n-Octane and Equimolar Mixture Water

Solubilities from 10 to 70°C

Water solubilities as a function of temperature are given in Table VII for 1-methylnaphthalene, n-octane and their equimolar binary hydrocarbon mixture. Equimolar activity coefficients calculated from the solubility determinations are given in Table VIII. No significant changes in the activity coefficients were observed as a function of

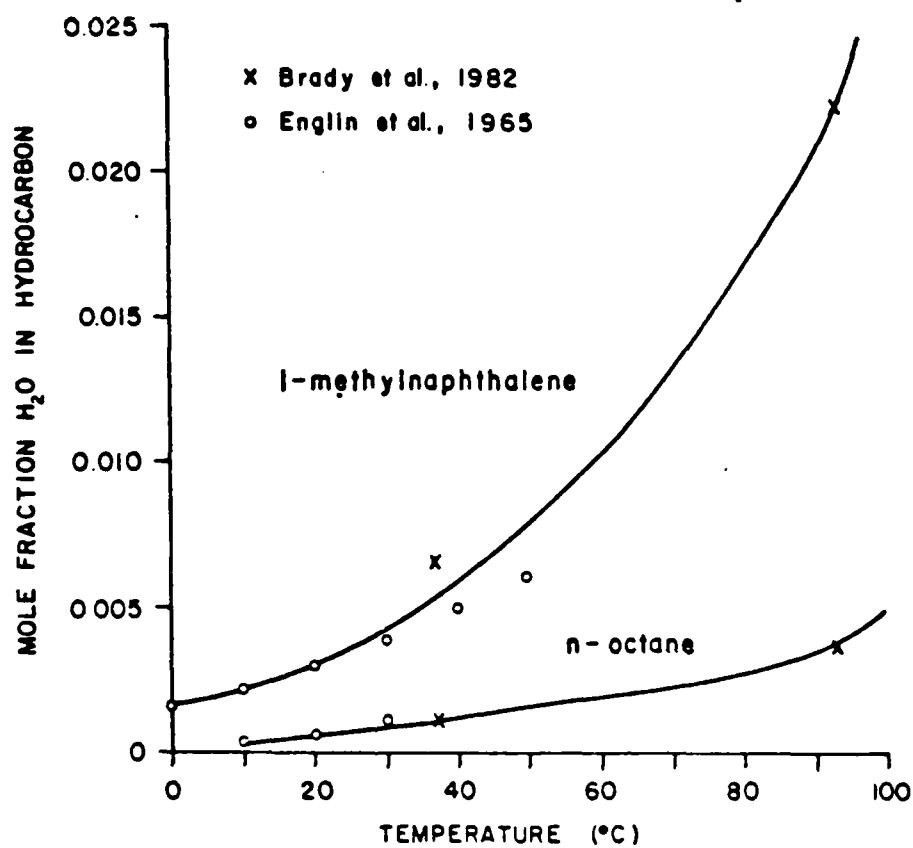


Figure 5. Solubility of water in single hydrocarbons, 1-methylnaphthalene and n-octane, as a function of temperature (Brady et al., 1982; Englin et al., 1965).

TABLE V. Activity coefficients in hydrocarbon phase for binary hydrocarbon as calculated from static vapor pressure (vp) and water solubility (ws) methods.

Mole Fraction A	vp $\gamma_{A(h)}$	ws $\gamma_{A(h)}$	vp $\gamma_{B(h)}$	ws $\gamma_{B(h)}$
n-octane (A) + 1-methylnaphthalene (B) at 20.0°C				
0.8961	1.01 (1.01) ^a	1.03 ± 0.12 ^b	2.41 (2.39)	2.50 ± 0.15
0.7960	1.05 (1.05)	1.04 ± 0.06	1.99 (1.98)	2.08 ± 0.10
0.6966	1.11 (1.10)	1.09 ± 0.07	1.70 (1.69)	1.74 ± 0.07
0.5037	1.30 (1.30)	1.33 ± 0.09	1.33 (1.33)	1.39 ± 0.08
0.3037	1.69 (1.68)	1.62 ± 0.11	1.11 (1.12)	1.16 ± 0.06
0.1856	2.07 (2.07)	2.10 ± 0.17	1.04 (1.04)	1.05 ± 0.05
0.0990	2.48 (2.48)	2.55 ± 0.14	1.01 (1.01)	1.03 ± 0.05
n-octane (A) + 1-methylnaphthalene (B) at 70.0°C				
0.8945	1.01	1.04 ± 0.05	2.11	2.14 ± 0.04
0.7906	1.04	1.09 ± 0.06	1.79	1.74 ± 0.03
0.6881	1.09	1.10 ± 0.04	1.56	1.56 ± 0.03
0.5000	1.25	1.34 ± 0.03	1.28	1.30 ± 0.01
0.2944	1.58	1.60 ± 0.05	1.10	1.11 ± 0.03
0.2040	1.82	1.96 ± 0.05	1.05	1.06 ± 0.02
0.1034	2.21	2.27 ± 0.08	1.01	1.01 ± 0.02
tetralin (A) + methylcyclohexane (B) at 20.0°C				
0.8976	1.01	1.02 ± 0.01	1.47	1.45 ± 0.02
0.8009	1.02	1.04 ± 0.01	1.36	1.35 ± 0.03
0.6985	1.04	1.06 ± 0.01	1.26	1.25 ± 0.02
0.5043	1.12	1.13 ± 0.01	1.14	1.14 ± 0.01
0.2926	1.26	1.29 ± 0.01	1.05	1.05 ± 0.01
0.2017	1.36	1.38 ± 0.02	1.03	1.02 ± 0.01
0.0966	1.52	1.52 ± 0.02	1.01	1.00 ± 0.01
ethylbenzene (A) + n-octane (B) at 20.0°C				
0.8979	1.01	1.00 ± 0.04	1.55	1.60 ± 0.09
0.8009	1.03	1.02 ± 0.03	1.38	1.33 ± 0.05
0.6964	1.07	1.06 ± 0.05	1.24	1.23 ± 0.09
0.5021	1.16	1.13 ± 0.03	1.09	1.04 ± 0.05
0.3024	1.28	1.24 ± 0.04	1.02	0.96 ± 0.06
0.2018	1.33	1.34 ± 0.04	1.01	0.96 ± 0.05
0.1213	1.36	1.33 ± 0.03	1.00	0.99 ± 0.07

^aValues in parentheses are from the mixture's second vapor pressure experiment.

^b95% Confidence limits for the mean.

TABLE VI. UNIFAC calculated activity coefficients for a 1-methylnaphthalene (A) + n-octane (B) mixture (9:1 mole fraction ratio), with and without water present in the hydrocarbon phase, at 70 and 150°C. Water content is estimated based upon the work of Eglin et al. (1965) and Brady et al. (1982).

<u>Temperature</u>	<u>Mole Fraction H₂O</u>	<u>$\gamma_{A(h)}$</u>	<u>$\gamma_{B(h)}$</u>	<u>$\gamma_{H_2O(h)}$</u>
70°C	0.012	1.009	1.974	233.8
	0.000	1.008	1.970	-
150°C	0.063	1.028	1.871	69.5
	0.000	1.008	1.851	-

TABLE VII. Water solubility of n-octane (OCT), 1-methylnaphthalene (MN) and their equimolar mixture as a function of temperature.

<u>Temperature</u>	<u>Solubility (mg/L; $\bar{x} \pm SD$)</u>		<u>Equimolar Mixture</u>	
	<u>Pure MN</u>	<u>Pure OCT</u>	<u>MN</u>	<u>OCT</u>
10.0°C	25.8 \pm 0.1	0.836 \pm 0.007	17.2 \pm 0.1	0.572 \pm 0.008
20.0°C	28.9 \pm 0.1	0.815 \pm 0.011	19.5 \pm 0.1	0.553 \pm 0.019
30.0°C	35.6 \pm 0.2	0.836 \pm 0.008	23.3 \pm 0.2	0.560 \pm 0.013
40.0°C	42.6 \pm 0.3	0.876 \pm 0.006	27.9 \pm 0.1	0.559 \pm 0.010
50.0°C	53.7 \pm 0.5	1.07 \pm 0.01	35.1 \pm 0.3	0.685 \pm 0.005
60.0°C	68.8 \pm 0.8	1.30 \pm 0.02	44.7 \pm 0.2	0.885 \pm 0.022
70.0°C	89.8 \pm 0.3	1.79 \pm 0.02	58.4 \pm 0.3	1.20 \pm 0.02

TABLE VIII. Hydrocarbon phase activity coefficients as a function of temperature for an equimolar n-octane (A) + 1-methylnaphthalene (B) mixture calculated from water solubility measurements.

<u>Temperature</u>	<u>$\gamma_{A(h)} (\pm 95 \% \text{ CL})$</u>	<u>$\gamma_{B(h)} (\pm 95 \% \text{ CL})$</u>
10.0°C	1.37 \pm 0.02	1.33 \pm 0.01
20.0°C	1.36 \pm 0.05 (1.32) ^a	1.34 \pm 0.01 (1.31)
30.0°C	1.34 \pm 0.04	1.31 \pm 0.01
40.0°C	1.28 \pm 0.03	1.31 \pm 0.01
50.0°C	1.28 \pm 0.02	1.30 \pm 0.02
60.0°C	1.36 \pm 0.04	1.30 \pm 0.02
70.0°C	1.34 \pm 0.04 (1.25)	1.30 \pm 0.01 (1.28)

^aValues in parentheses are activity coefficients calculated from vapor pressure data.

temperature. The vapor pressure derived activity coefficients did decrease slightly with temperature but this change was not enough to be detected by the water solubility method.

The solubilities generally increase as a function of temperature. The solubility of n-octane, however, decreased from 10 to 20°C. Pure 1-methylnaphthalene and pure n-octane solubilities (10 to 60°C) in Table VII were converted to $\Delta G_{i,s}^{\circ}$ values. Polynomial regressions were run on the two sets of $\Delta G_{i,s}^{\circ}$ values. The resulting polynomials were:

$$\begin{aligned} \text{1-methyl-naphthalene: } \Delta G_{i,s}^{\circ} (\text{kJ mol}^{-1}) &= -30.77 + 0.3527(T) - 4.905 \times 10^{-4}(T)^2 \\ \text{n-octane: } \Delta G_{i,s}^{\circ} (\text{kJ mol}^{-1}) &= -80.44 + 0.6780(T) - 9.262 \times 10^{-4}(T)^2 \end{aligned}$$

$\Delta G_{i,s}^{\circ}$ functions in conjunction with equations (20) and (21) were used to calculate $\Delta G_{i,s}^{\circ}$, $\Delta H_{i,s}^{\circ}$ and $\Delta S_{i,s}^{\circ}$ values at 25°C, which are listed below along with literature values.

<u>$\Delta G_{i,s}^{\circ} (\text{kJ mol}^{-1})$</u>	<u>$\Delta H_{i,s}^{\circ} (\text{kJ mol}^{-1})$</u>	<u>$T\Delta S_{i,s}^{\circ} (\text{kJ mol}^{-1})$</u>	<u>Reference</u>
n-octane:			
39.4	1.9	-37.5	This Work
37.7	1.7	-36.1	Nelson and De Ligny (1968)
1-methylnaphthalene:			
30.8	12.8	-18.0	This Work
30.9	22.4	-8.5	Calculated from Schwarz (1977)

There is fairly good agreement in the n-octane values and some discrepancies within the 1-methylnaphthalene values. Limited information on solution processes can be gained from standard state thermodynamic parameters. Some statements might be made from comparison of the values of many different compounds, and those statements might be of limited utility.

The decrease in the solubility of n-octane from 10 to 20°C was also observed by Nelson and De Ligny (1968) from 5 to 25°C. A similar decrease in solubility was observed by Whitehouse (1984) for 1,2-benzanthracene from 4 to 12°C. Decreasing solubility with increasing temperature is a curious feature since almost all other hydrocarbons appear to increase solubility with increasing temperature. If the solubility decreases with increasing temperature then the dissolution process must be exothermic. At higher temperatures the heat of solution may change sign and entropy effects may become important.

6. Summary

There is no significant difference between $\gamma_{i(h)}$ values calculated by the static vapor pressure method and $\gamma_{i(h)}$ values determined by water solubility measurements and equation (2). This indicates that $\gamma_{i(h)}$ values are sufficient to explain the positive deviations in solubility and that $\gamma_{i(w)}$ equals $\gamma_{i(w)}^0$ within the precision of water solubility measurements. This conclusion is a clear contradiction to the conclusions drawn by Leinonen and Mackay (1973) and Leinonen (1976), but is in agreement with the results of Green and Frank (1979). Equation (2) is adequate for explaining the water solubility of binary hydrocarbon mixtures.

Activity coefficients do not change much as a function of temperature as seen in the equimolar 1-methylnaphthalene + n-octane solubility results. Water in the hydrocarbon phase at 70°C does not appear to affect the activity coefficient values. UNIFAC calculations using data on the solubility of water in the hydrocarbon phase suggests that the presence of water in a 1-methylnaphthalene + n-octane binary mixture does not significantly affect hydrocarbon phase activity coefficients from 70 to 150°C. The presence of a significant amount of water in the hydrocarbon phase may affect the validity of the first assumption leading to equation (2) (i.e., $x_{i(h)}^0$ and $\gamma_{i(h)}^0$ are both unity). At 150°C, $x_{i(h)}^0$ would be approximately 0.94 and $\gamma_{i(h)}^0$ would be approximately 1.03 for 1-methylnaphthalene. $x_{i(h)}^0$ and $\gamma_{i(h)}^0$ would partially offset each other in terms of their resulting affect on $x_{i(w)}$.

Hydrocarbon water solubility generally increases as a function of temperature. Decreasing solubility with increasing temperature for

n-octane in the 10 to 20°C range indicates that it is an exothermic process in that temperature range. Little information on the solution process is gained from the calculated standard state thermodynamic parameter values.

ADDITIONAL SYSTEM STUDIES

Additional hydrocarbon mixture + water systems were examined to provide further insight into the aqueous solution behavior of hydrocarbon fuels. Aromatic + aliphatic binary hydrocarbon mixtures were selected to be representative of more complex mixtures while being more simple to analyze and interpret. The solubilities of two 12-component simulated jet fuel mixtures were examined to more closely approximate the actual fuels. Methods for predicting the simulated jet fuel mixture solubilities were investigated. The solubility of a binary hydrocarbon mixture in the presence of dissolved salts and dissolved organic material was determined to assess the effect of these dissolved materials on the equilibrium aqueous solubility of liquid hydrocarbon mixtures.

1. Additional Solubilities of Binary Hydrocarbon Mixtures

a. Solubility Experiments Examining a Full Range of Mixture Compositions

The water solubilities over a full range of mixture compositions (approximate mole fraction ratios of 1:9, 1:3, 1:1, 3:1 and 9:1) were determined for the following binary hydrocarbon mixtures: 1-methylnaphthalene + 1,4-dimethylnaphthalene; 1-methylnaphthalene + naphthalene; 1-methylnaphthalene + methylcyclohexane; n-octane + methylcyclohexane; n-octane + 1-methylnaphthalene (replication of this binary mixture is reported above); n-octane + naphthalene and n-octane + 1,4-dimethylnaphthalene. Incubators were used for these solubility

experiments only. The 97% 1-methylnaphthalene was used only for these experiments; 99% purity was located after these experiments were conducted.

The hypothetical supercooled liquid solubility for pure naphthalene was calculated using heat capacity and heat of fusion data in American Petroleum Institute Publication 707 (1978) by a method described by Hildebrand et al. (1970). Mixtures without a solid phase (predominantly naphthalene) were examined exclusively.

Equilibrium water solubility results are shown in Figures 6 through 12. The horizontal axis in each corresponds to the mole fraction of one component in the binary mixture, and the two vertical axes in each correspond to aqueous phase concentrations. The straight lines have intercepts giving the measured pure component solubilities, and represent ideal solution behavior. Curves are drawn through the means of the mixture solubilities using a cubic spline curve fitting routine. Concentration ranges ($\bar{x} \pm 1$ SD) are represented by the error bars.

Assumptions of ideal solution behavior hold well when predicting aqueous concentrations resulting from equilibration with binary mixtures containing compounds that are structurally similar (i.e., n-octane + methylcyclohexane, 1-methylnaphthalene + naphthalene and 1-methylnaphthalene + 1,4-dimethylnaphthalene). Significant deviations from ideality occur when the two compounds differ structurally (i.e., the aliphatic + aromatic pairs: 1-methylnaphthalene + n-octane, 1-methylnaphthalene + methylcyclohexane, n-octane + 1,4-dimethylnaphthalene and n-octane + naphthalene). The greatest deviations from ideal solution behavior exist with the 1-methylnaphthalene + n-octane

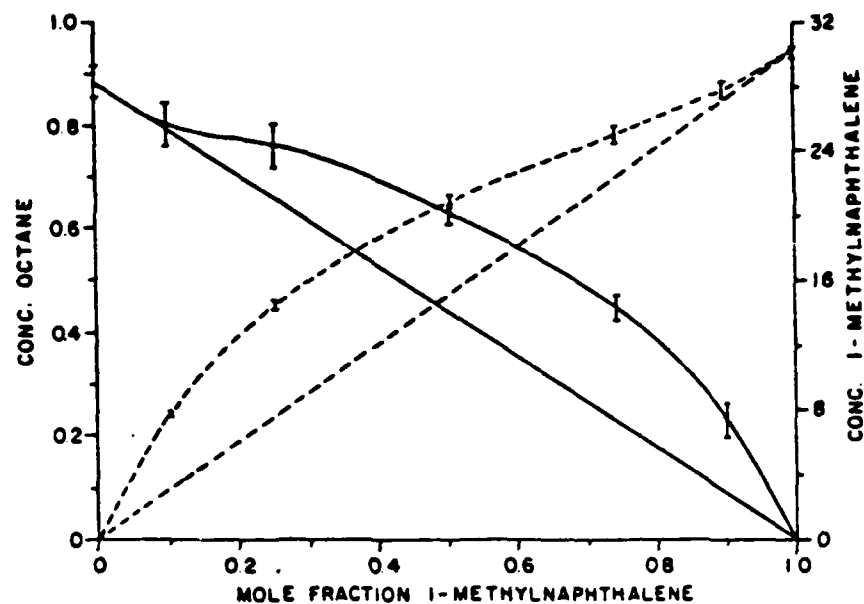


Figure 6. Water solubility results for n-octane + 1-methylnaphthalene system. Solid and dashed lines correspond to the left and right axes, respectively. Units of concentration are mg/L.

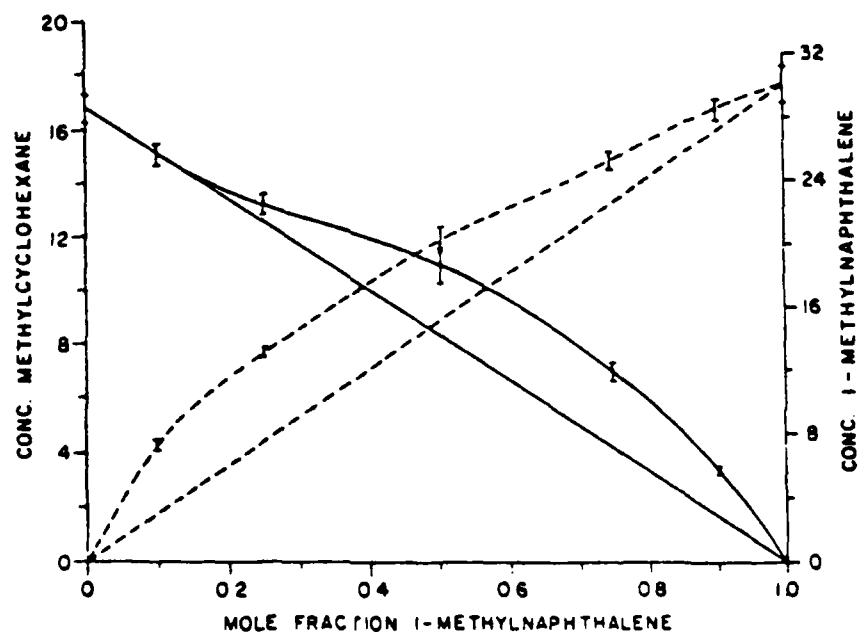


Figure 7. Water solubility results for methylcyclohexane + 1-methylnaphthalene system. Solid and dashed lines correspond to the left and right axes, respectively. Units of concentration are mg/L.

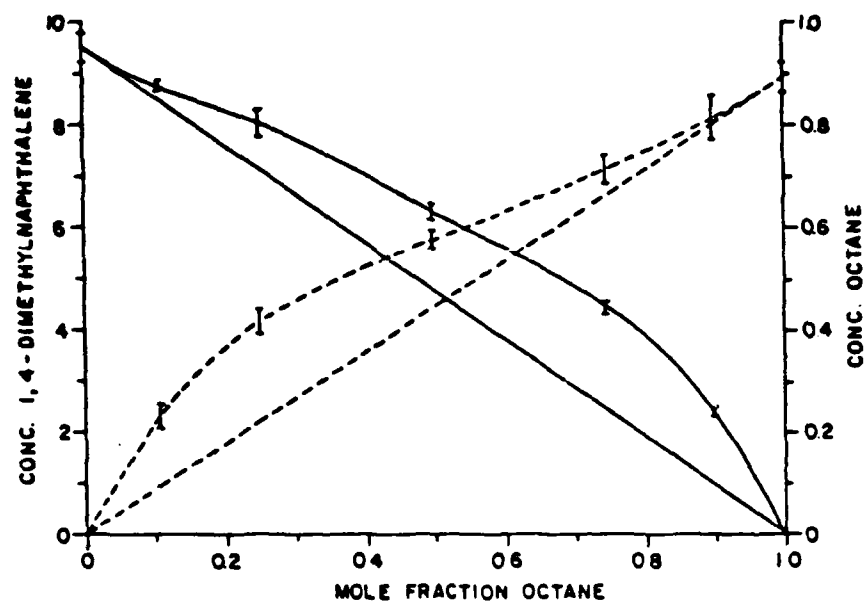


Figure 8. Water solubility results for 1,4-dimethylnaphthalene + n-octane system. Solid and dashed lines correspond to the left and right axes, respectively. Units of concentration are mg/L.

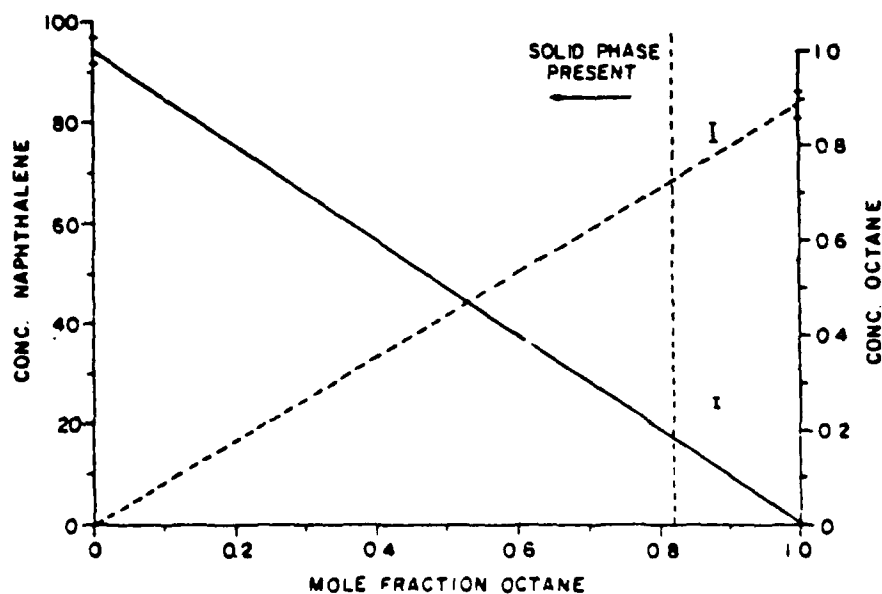


Figure 9. Water solubility results for naphthalene + n-octane system. Solid and dashed lines correspond to the left and right axes, respectively. Units of concentration are mg/L.

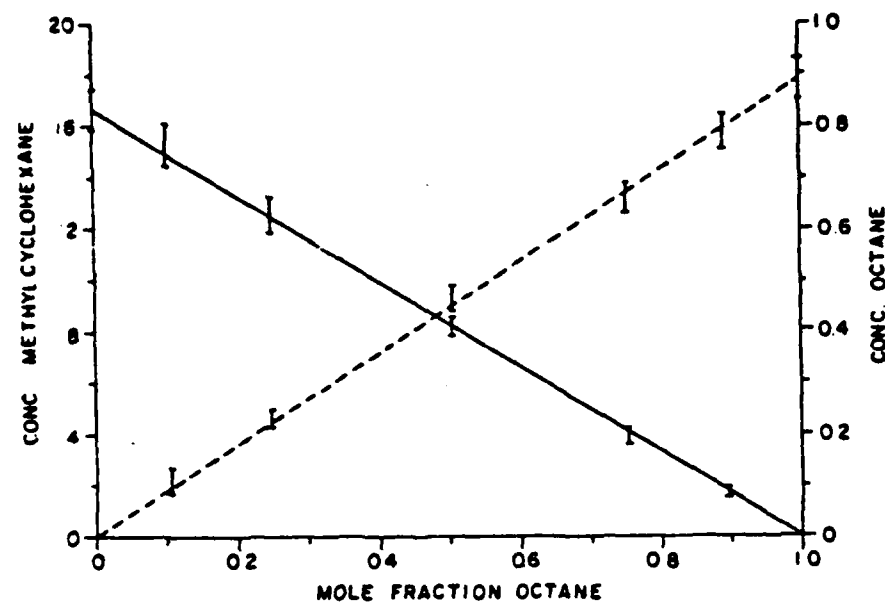


Figure 10. Water solubility results for methylcyclohexane + n-octane system. Solid and dashed lines correspond to the left and right axes, respectively. Units of concentration are mg/L.

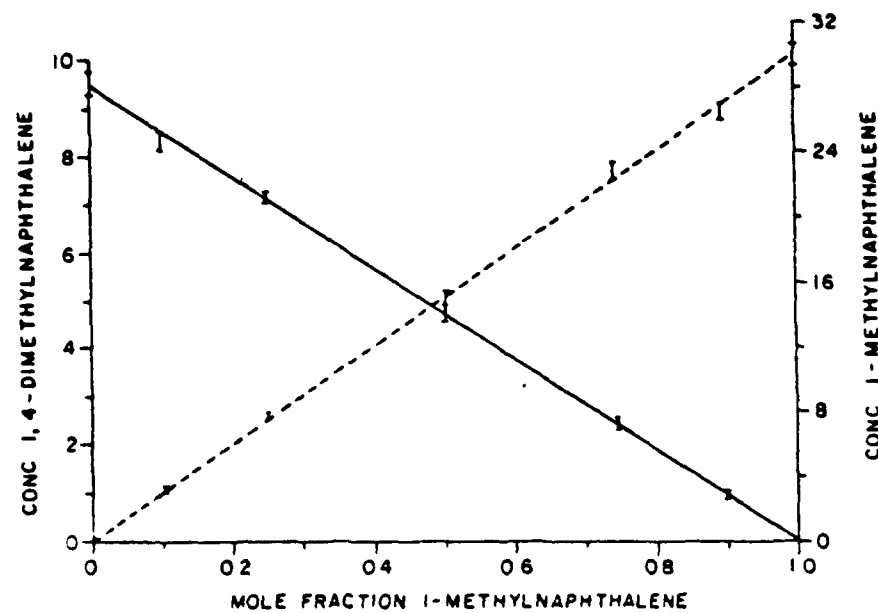


Figure 11. Water solubility results for 1,4-dimethylnaphthalene + 1-methylnaphthalene system. Solid and dashed lines correspond to the left and right axes, respectively. Units of concentration are mg/L.

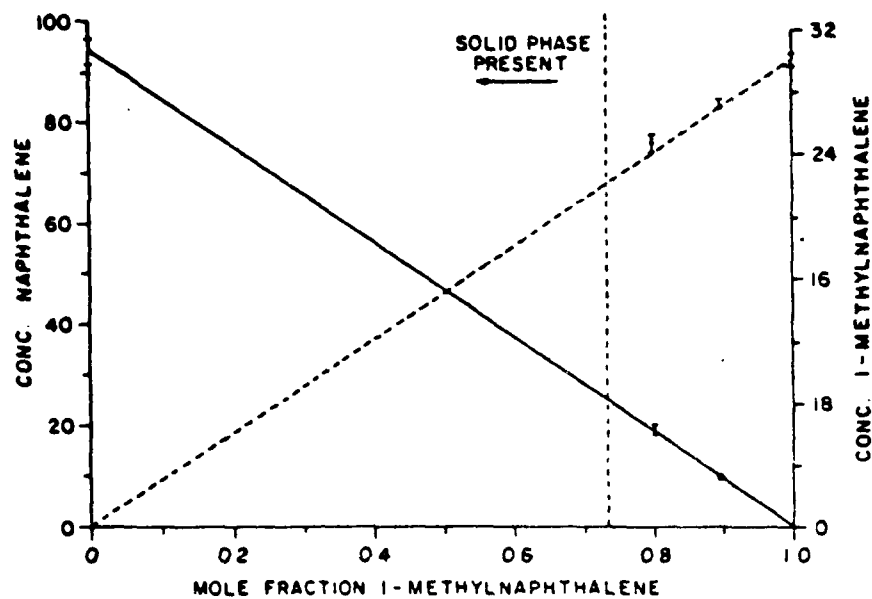


Figure 12. Water solubility results for naphthalene + 1-methylnaphthalene system. Solid and dashed lines correspond to left and right axes, respectively. Units of concentration are mg/L.

binary mixtures. 1-Methylnaphthalene + n-octane results obtained using incubators agree well with the results using the water bath given in Table IV.

b. Solubility Experiments Examining an Abbreviated Range of Compositions for 1-Methylnaphthalene + n-Alkane Mixtures

The water solubilities of 1-methylnaphthalene + n-alkane binary mixtures (approximate mole fraction ratios of 1:9, 1:4 and 3:7) were measured to examine the role of molecular structure in determining the extent of non-ideal solution behavior. The low aromatic mole fraction portion of the total composition range was selected since it encompassed the aromatic/aliphatic ratio encountered in most petroleum-based fuels. The results of this series of experiments are shown in Figure 13, and are given as the observed 1-methylnaphthalene solubility divided by the ideal 1-methylnaphthalene solubility (i.e., $\gamma_{MN(h)}$ values).

The 1-methylnaphthalene + n-alkane binary pair solubilities show a continuous trend towards ideality as the n-alkane chain length increases. A similar trend appears to be present for benzene + n-alkane mixtures (see Figure 14) based upon vapor-liquid equilibria data found in the literature (Smith and Robinson, 1970; Jain, Gupta and Lark, 1970; Harris and Dunlop, 1970; Jain, Gupta and Lark, 1973; Jain and Lark, 1973). The benzene + n-heptane results of Jain, Gupta and Lark (1973) are inconsistent with the rest of the data in Figure 14 and may be in error. It appears that, for aromatic + n-alkane systems, G^E decreases as the n-alkane chain length increases. H^E , however, increases for these types of systems as the n-alkane chain-length

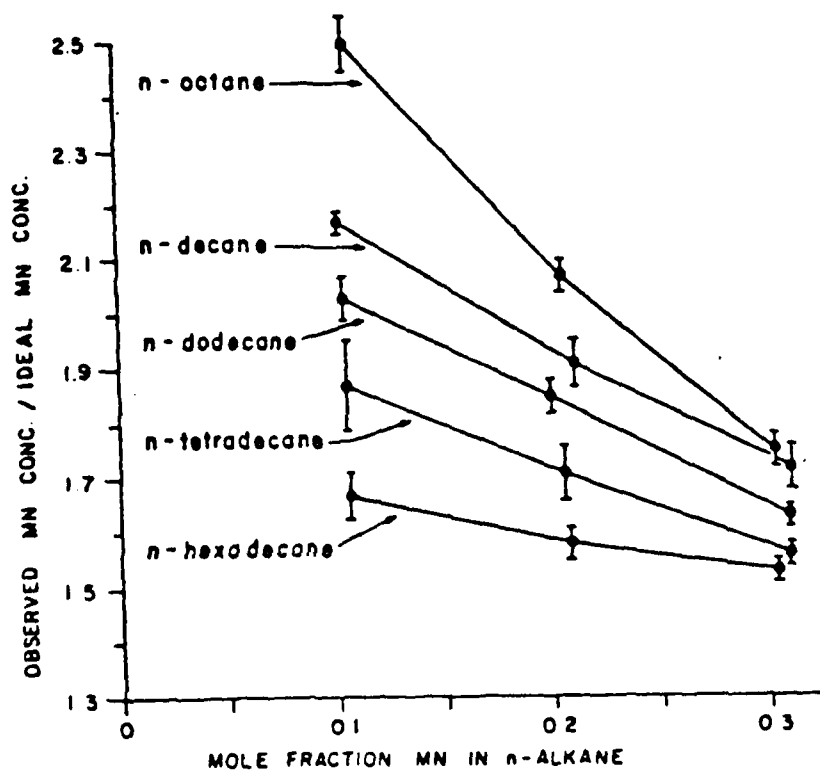


Figure 13. Quotients of 1-methylnaphthalene(MN) solubilities over their ideal solubilities for a series of MN + n-alkane binary mixtures. Error bars represent 90% confidence limits for the mean.

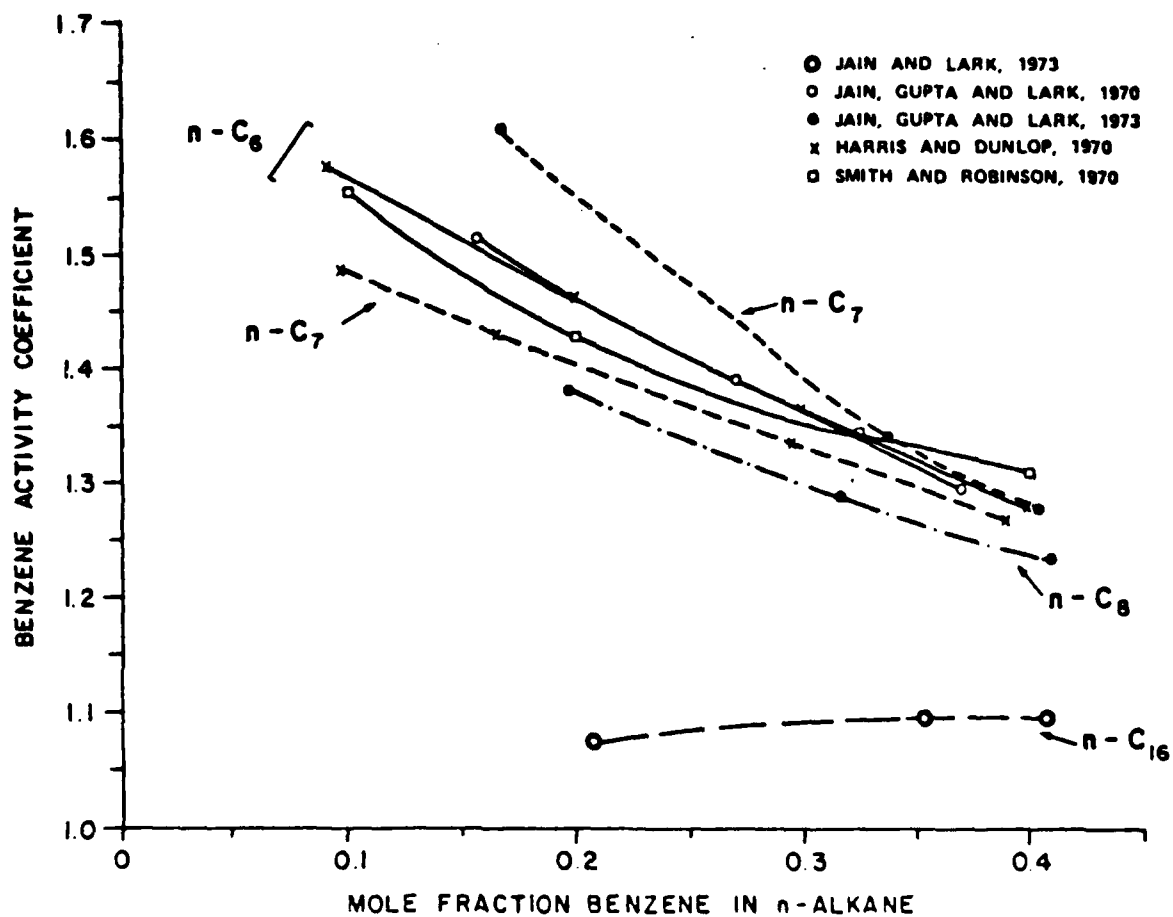


Figure 14. Benzene activity coefficient values for benzene + n-alkane systems at 25°C obtained from the literature.

increases (Diaz Pena and Menduina, 1974). The decrease in G^E thus appears to be due to an increase in S^E . Increasing S^E with increasing chain-length may be due to more possible configurations for the longer chain-length n-alkanes.

c. Solubility Experiments Examining an Abbreviated Range of Compositions for Aromatic + n-Octane Mixtures

The water solubilities of aromatic + n-octane binary mixtures (approximate mole fraction ratios of 1:9, 1:4 and 3:7) were determined to further examine the effect of structure on the extent of non-ideal behavior. The low aromatic mole fraction range was chosen since it encompasses the aromatic/aliphatic ratio of most petroleum-based fuels. The results are shown in Figure 15, and are given as the observed aromatic solubility divided by the ideal aromatic solubility (i.e., $Y_{i(h)}$ values for the aromatic components). The solubilities of the single hydrocarbons are given in Table X in the next section, except for those of phenylcyclohexane and n-hexylbenzene which are given in Table III.

The binary hydrocarbon mixtures containing naphthalenes have significantly greater non-ideal solubility behavior than those containing benzenes. It appears that the greater the aliphatic portion of the naphthalenes, the more ideal is the behavior. This trend is not completely adhered to with the benzenes examined.

2. Solubilities of 12-Component Simulated Jet Fuels

The components and compositions of the 12-component simulated JP-4 and JP-8 jet fuel mixtures were selected to be representative of actual JP-4 and JP-8 jet fuels. The compositions of the simulated jet fuels are given in Table IX. The single compound water solubilities at 20°C are given in Table X. The water solubilities at 20°C of the analyzable components of JP-4 and JP-8 simulated jet fuels are given in Table XI. The simulated jet fuels had a considerable amount of polar impurities. The effect of these impurities on the analysis of the components of interest is not known. Some of the component solubilities may be slightly in error (by as much as 5 to 10%). Considering the complex nature of these systems, this was considered to be reasonably good. Determination of the solubility of an actual fuel would have been far more difficult.

3. Methods for Predicting the Solubility of Liquid Hydrocarbon Mixtures

The results of the simulated jet fuel mixture solubility experiments were used to test four methods for predicting the solubility of liquid hydrocarbon mixtures. The conditions for predicting the solubility of 12-component mixtures are the same as for binary mixtures: the hydrocarbon phase composition must be known, the single compound solubilities must be known for those components which are dissolved in analyzable quantities and the $\gamma_{i(h)}$ must be known or predicted. Hydrocarbon phase composition and single compound solubilities are relatively easy to obtain. Hydrocarbon phase activity coefficients for multicomponent mixtures are more difficult to obtain or predict.

TABLE IX. Compositions of the 12-component simulated jet fuel mixtures.

<u>Component</u>	<u>Weight Percent</u>	<u>Mole Fraction</u>
<u>Simulated JP-4</u>		
toluene	3.05	0.04311
ethylbenzene	3.90	0.04785
n-butylbenzene	3.99	0.03879
tetralin	2.96	0.02922
1-methylnaphthalene	2.91	0.02666
1,4-dimethylnaphthalene	3.13	0.02613
methylcyclohexane	15.99	0.2123
n-octane	16.04	0.1830
n-decane	15.03	0.1377
n-undecane	12.39	0.1033
n-dodecane	10.71	0.08192
n-tridecane	9.90	0.06996
<u>Simulated JP-8</u>		
n-butylbenzene	3.08	0.03865
1,3,5-triethylbenzene	4.05	0.04198
tetralin	2.94	0.03744
1-methylnaphthalene	3.09	0.03661
1,4-dimethylnaphthalene	3.11	0.03355
2-ethylnaphthalene	4.05	0.04365
n-decane	7.81	0.09233
n-undecane	13.90	0.1497
n-dodecane	18.87	0.1864
n-tridecane	19.09	0.1742
n-tetradecane	12.61	0.1069
n-pentadecane	7.40	0.05859

TABLE X. Water solubilities of single hydrocarbons, used in simulated jet fuel mixtures, measured at 20°C.

<u>Compound</u>	<u>Solubility (mg/L, $\bar{x} \pm SD$)</u>
toluene	567 \pm 8
ethylbenzene	180 \pm 1
n-butylbenzene	13.3 \pm 0.2
1,3,5-triethylbenzene	3.47 \pm 0.02
tetralin	45.0 \pm 0.4
1-methylnaphthalene	30.2 \pm 0.3
1,4-dimethylnaphthalene	9.47 \pm 0.14
2-ethylnaphthalene	9.21 \pm 0.09
methylcyclohexane	16.6 \pm 0.4
n-octane	0.884 \pm 0.011

TABLE XI. Water solubilities of analyzable components of JP-4 and JP-8 simulated jet fuels and $\gamma_{i(h)}$ values calculated from these measurements. Concentration units are mg/L.

Component (i)	Solubility ($\bar{x} \pm SD$)	$\gamma_{i(h)} (\pm 95 \% CL)$
<u>Simulated JP-4</u>		
toluene	28.3 ± 0.5	1.16 ± 0.03
ethylbenzene	10.6 ± 0.1	1.23 ± 0.01
n-butylbenzene	0.624 ± 0.007	1.21 ± 0.02
tetralin	1.90 ± 0.02	1.45 ± 0.02
1-methylnaphthalene	1.80 ± 0.02	2.24 ± 0.03
1,4-dimethylnaphthalene	0.536 ± 0.004	2.17 ± 0.04
methylcyclohexane	3.50 ± 0.05	0.99 ± 0.03
n-octane	0.173 ± 0.003	1.07 ± 0.02
Total	$47.3 \quad (43.8)^a$	
<u>Simulated JP-8</u>		
n-butylbenzene	0.613 ± 0.017	1.19 ± 0.04
1,3,5-triethylbenzene	0.164 ± 0.002	1.12 ± 0.02
tetralin	2.25 ± 0.04	1.34 ± 0.03
1-methylnaphthalene	2.11 ± 0.06	1.90 ± 0.06
1,4-dimethylnaphthalene	0.629 ± 0.005	1.98 ± 0.04
2-ethylnaphthalene	0.682 ± 0.006	1.70 ± 0.02
Total	6.45	

^aAromatic components only.

The use of 'enhancement factors' (Leinonen, 1976) was the only method for predicting the solubility of multicomponent hydrocarbon mixtures found in the literature. Instead of $\gamma_{i(h)}$ values, Leinonen used enhancement factors dependent upon compound type. The results of the enhancement factor method for predicting the solubility of the simulated jet fuels are given in Table XII. The method over-predicted individual solute concentrations by as much as 95% and total JP-4 solubility by 78%. 'Enhancement factors' suggested by Leinonen (1976) predict unrealistically high solubility values and are little better than using the assumption of ideal solution behavior.

A graphical method of predicting multicomponent $\gamma_{i(h)}$ values was developed using the data in Figure 15 and the simulated jet fuel data. It was found that if vertical lines (dashed lines in Figure 15) were drawn at the mole fractions that corresponded to the mole fraction of the total aromatics in the fuel mixture, then the intersections of the dashed lines and the solid lines provided reasonably good estimates for $\gamma_{i(h)}$. This method works only for the aromatic components. The results of the graphical method of predicting $\gamma_{i(h)}$ values are given in Table XIII. Predicted solubilities are quite good considering possible analytical errors in the fuel mixture solubilities.

The graphical method is empirical and its effectiveness is curious. It is also curious that the n-octane + aromatic binary mixture data in Figure 15 works reasonably well because n-octane was only one of six aliphatic components in JP-4 and was not present in JP-8. It may be that Bronsted's principle of congruence (Bronsted and Koefoed, 1948) applies to the aliphatic portion of the mixtures, so that interaction effects due to the aliphatic portion can be

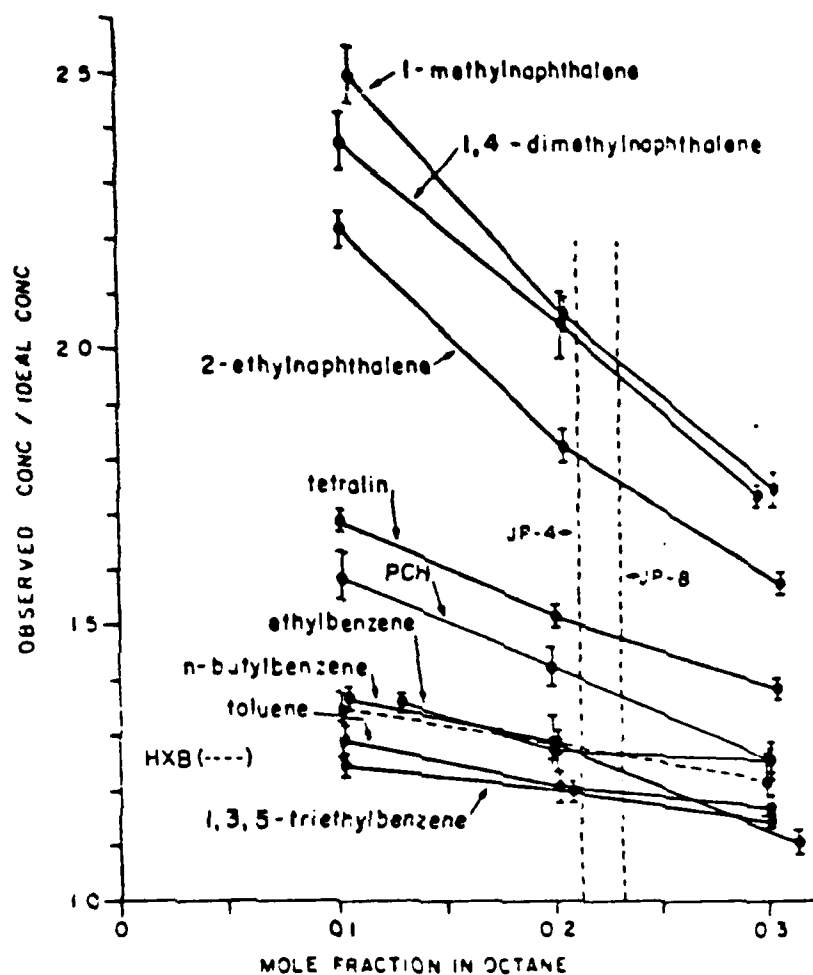


Figure 15. Quotients of observed aromatic component solubilities over their ideal solubilities for a series of aromatic + n-octane binary mixtures. Error bars represent the 90% confidence limits for the mean. The intersections of the solid and vertical dashed lines are used in the graphical method for predicting multicomponent mixture $Y_{i(h)}$ values as described later in the text.

TABLE XII. Predicted solubilities for simulated jet fuel mixtures using the 'enhancement factor' concept of Leinonen (1976) in place of $\gamma_{i(h)}$ values. Concentration units are mg/L.

<u>Component (i)</u>	<u>Enhancement Factor, e_i</u>	<u>Predicted Solubility^a</u>	<u>% Difference From Observed</u>
<u>Simulated JP-4</u>			
toluene	2.2	53.8	+90
ethylbenzene	2.2	18.9	+78
n-butylbenzene	2.2	1.13	+81
tetralin	2.2	2.89	+52
1-methylnaphthalene	2.2	1.77	-1.7
1,4-dimethylnaphthalene	2.2	0.544	+1.5
methylcyclohexane	1.4	4.93	+41
n-octane	1.4	0.226	+31
Total		84.2	+78
<u>Simulated JP-8</u>			
n-butylbenzene	2.2	1.13	+84
1,3,5-triethylbenzene	2.2	0.320	+95
tetralin	2.2	3.71	+65
1-methylnaphthalene	2.2	2.43	+15
1,4-dimethylnaphthalene	2.2	0.699	+11
2-ethylnaphthalene	2.2	0.884	+30
Total		9.17	+42

^aUsing equation (2) with e_i in place of $\gamma_{i(h)}$.

TABLE XIII. Predicted solubilities for simulated jet fuel mixtures using graphical method for predicting $\gamma_{i(h)}$ values. Concentration units are mg/L.

<u>Component</u>	<u>Predicted $\gamma_{i(h)}$</u>	<u>Predicted Solubility^a</u>	<u>% Difference From Observed</u>
<u>Simulated JP-4</u>			
toluene	1.21	29.6	+4.6
ethylbenzene	1.28	11.0	+3.8
n-butylbenzene	1.27	0.655	+5.0
tetralin	1.50	1.97	+3.7
1-methylnaphthalene	2.04	1.64	-8.9
1,4-dimethylnaphthalene	2.02	0.500	-6.7
methylcyclohexane	b		
n-octane	b		
Total		<u>45.4^c</u>	+3.7 ^c
<u>Simulated JP-8</u>			
n-butylbenzene	1.24	0.637	+3.9
1,3,5-triethylbenzene	1.19	0.173	+5.5
tetralin	1.48	2.49	+10.7
1-methylnaphthalene	1.98	2.19	+3.8
1,4-dimethylnaphthalene	1.96	0.623	-1.0
2-ethylnaphthalene	1.76	<u>0.708</u>	+3.8
Total		6.82	+5.7

^aUsing equation (2).

^b $\gamma_{i(h)}$ can not be predicted from data in Figure 15.

^cUsing aromatic components only.

approximated by the mean n-alkane chain length. Although the mean alkane chain length is about n-nonane for JP-4 and about n-dodecane for JP-8, the predicted solubilities are not much better for JP-4 than JP-8. This may be because the 1-methylnphtalene $\gamma_{i(h)}$ values at the 0.2 mole fraction level in Figure 13 using n-octane and n-dodecane are approximately 2.1 and 1.9, respectively. The difference in the predicted solubility using these two values is only 10%.

A numerical method for predicting activity coefficients in multicomponent systems was presented by King (1969). For this method, activity coefficient information is required for each possible binary pair within the multicomponent system. For example, assume a four component system of A, B, C and D. The activity coefficient for A can be obtained using:

$$\ln \gamma_A = x_B^2 b_{AB} + x_C^2 b_{AC} + x_D^2 b_{AD} + x_B x_C (b_{AB} + b_{AC} - b_{BC}) \\ + x_B x_D (b_{AB} + b_{AD} - b_{BD}) + x_C x_D (b_{AC} + b_{AD} - b_{CD}) \quad (26)$$

, where the coefficients b_{AB} , b_{AC} , etc. are obtained from the appropriate binary system activity coefficients, and are given for the binary system Q + P:

$$b_{QP} = \frac{\ln \gamma_Q}{x_P^2} \quad (27)$$

The other multicomponent activity coefficients are obtained using an expression of the form of equation (22). Equation (22) can be expanded for a multicomponent system of any size, but it is necessary to have reasonable activity coefficient information for all the possible binary mixtures within the multicomponent system. Note that only one of the activity coefficients for each binary mixture is needed.

Binary mixture activity coefficients necessary for the simulated jet fuels were obtained as follows: Aliphatic + aliphatic or aromatic + aromatic binary pairs were given activity coefficients of 1.00. For aromatic + aliphatic binary pairs, the aromatic component's activity coefficient was estimated using Figures 13 and 15. Extrapolations were made when the mole fraction needed was outside of the mole fraction range experimentally examined. For aromatic + aliphatic mixtures in which n-undecane, n-tridecane and n-pentadecane was the aliphatic component, values were interpolated normal to the curves in Figure 13. The following equations were used to estimate aromatic component activity coefficients in aromatic + aliphatic binary mixtures that did not contain either 1-methylnaphthalene or n-octane, using binary mixture data that did.

$$\gamma_{i(h)} = 1.00 + z_{i(h)} \quad (28)$$

$$z_{j(h)} = z_{j(h)}^* \left(\frac{z_{k(h)}^*}{z_{k(h)}^*} \right) \quad (29)$$

The subscripts j and k correspond to the aromatic component of interest and 1-methylnaphthalene, respectively. The superscript, *, signifies that n-octane is the aliphatic component in the mixture. The aromatic mole fraction is the same throughout the calculation.

The results of the method of King (1969) for predicting $\gamma_{i(h)}$ values for the simulated jet fuel mixtures are given in Table XIV. The predicted solubilities were all within 10% of the observed solubilities.

TABLE XIV. Predicted solubilities for simulated jet fuel mixtures using the numerical method of King (1969) for predicting $\gamma_{i(h)}$ values. Concentration units are in mg/L.

<u>Component (i)</u>	<u>Predicted $\gamma_{i(h)}$</u>	<u>Predicted Solubility^a</u>	<u>% Difference From Observed</u>
<u>Simulated JP-4</u>			
toluene	1.15	28.1	-0.7
ethylbenzene	1.22	10.5	-0.9
n-butylbenzene	1.17	0.604	-3.2
tetralin	1.46	1.92	+1.1
1-methylnaphthalene	2.10	1.69	-6.1
1,4-dimethylnaphthalene	2.03	0.502	-6.3
methylcyclohexane	1.03	3.63	+3.7
n-octane	1.03	0.167	-3.5
Total		47.1 (43.3) ^b	-0.6 (-1.1) ^b
<u>Simulated JP-8</u>			
n-butylbenzene	1.11	0.571	-6.9
1,3,5-triethylbenzene	1.06	0.154	-6.1
tetralin	1.35	2.27	+0.9
1-methylnaphthalene	1.87	2.07	-1.9
1,4-dimethylnaphthalene	1.80	0.572	-9.1
2-ethylnaphthalene	1.66	0.667	-2.2
Total		6.30	-2.3

^aUsing equation (2).

^bUsing aromatic components only.

The use of UNIFAC to predict multicomponent mixture activity values only requires knowledge of the mixture's composition. The UNIFAC calculated activity coefficient results for the simulated jet fuel mixtures are given in Table XV. The predicted solubilities were generally within 10% of the observed solubilities except for some of the substituted naphthalenes. This may be because naphthalenes were not used in setting up UNIFAC group-contribution tables. UNIFAC is more convenient to use than the graphical or numerical (King, 1969) methods since it is easily and rapidly done with a computer with less experimental data.

4. Solubility of a Binary Hydrocarbon Mixture in York River Water and Artificial Seawater - Effects of Dissolved Salts and Dissolved Organic Material

The aqueous solubility of a methylcyclohexane + 1-methylnaphthalene binary mixture (0.2015 mole fraction 1-methylnaphthalene) was determined in organic-free deionized water, 14 parts per thousand (ppt) artificial seawater and 14 ppt, 0.2 micron filtered, York River water to determine the effects of dissolved salts and a natural level of dissolved organic material (DOM) on the aqueous solution behavior of a hydrocarbon mixture. The DOM concentrations in the York River water have been determined at VIMS to be in the 1 - 10 mg/L range.

A liter of 30 ppt artificial seawater was prepared by dissolving the following salts in deionized water: 23.16 g NaCl, 2.38 g MgSO_4 , 4.02 g $\text{MgCl} \cdot 6\text{H}_2\text{O}$, 1.45 g CaCl_2 , 0.74 g KCl, 100 mg KBr, 25 mg H_3BO_3 and 50 mg NaHCO_3 . The solution was 0.2 micron filtered and diluted to York

TABLE XV. Predicted solubilities for simulated jet fuel mixtures using UNIFAC predicted $\gamma_{i(h)}$ values. Concentration units are mg/L.

<u>Component (i)</u>	<u>Predicted $\gamma_{i(h)}$</u>	<u>Predicted Solubility^a</u>	<u>% Difference From Observed</u>
<u>Simulated JP-4</u>			
toluene	1.22	29.8	+5.4
ethylbenzene	1.20	10.3	-2.8
n-butylbenzene	1.18	0.609	-2.4
tetralin	1.33	1.75	-7.9
1-methylnaphthalene	1.89	1.50	-16.7
1,4-dimethylnaphthalene	1.74	0.431	-19.6
methylcyclohexane	0.97	3.42	-2.3
n-octane	1.03	0.167	-3.5
Total		48.0 (44.4) ^b	+1.3 (+1.4) ^b
<u>Simulated JP-8</u>			
n-butylbenzene	1.14	0.586	-4.4
1,3,5-triethylbenzene	1.10	0.160	-2.4
tetralin	1.27	2.14	-4.9
1-methylnaphthalene	1.78	1.97	-6.6
1,4-dimethylnaphthalene	1.72	0.546	-13.2
2-ethylnaphthalene	1.65	0.663	-2.8
Total		6.07	-5.9

^aUsing equation (2).

^bUsing aromatic components only.

River water salinity prior to use. Salinities were measured with a hand-held refractometer (American Optical Corp.).

The results of this experiment are given in Table XVI. Water containing 14 ppt dissolved salts, both artificial and natural, decreased the solute concentrations by approximately 15%. This observation is in general agreement with the degree of solubility reduction found for pure hydrocarbons by Gordon and Thorne (1967), Sutton and Calder (1975) and Eganhouse and Calder (1976). Solute concentrations ratios were the same for deionized water and saline water samples, indicating that the basic features of mixture solubility behavior did not change. There was no significant difference between the artificial seawater and York River water samples, indicating that this natural level of DOM did not significantly affect the equilibrium solubility behavior of the mixture. This is expected from the results of Hashimoto et al. (1984) and Whitehouse (1985). The York River water DOM may be partitioning into the hydrocarbon phase, thus minimizing the possible effects of the DOM.

5. Solubility of Hydrocarbon Mixtures Containing o-Dichlorobenzene

Groundwater contamination situations exist in which hydrocarbon fuels have been released along with small amounts of chlorinated cleaning solvents and from an organic phase that lies on top of the water table. The mixtures examined in these experiments were selected as being a simple representation of this type of contamination situation.

The solubilities of the tetralin + methylcyclohexane + o-dichlorobenzene mixtures examined are given in Table XVII. The

TABLE XVI. Water solubility of a methylcyclohexane(MCH) + 1-methyl-naphthalene(MN) (0.2015 mole fraction MN) mixture in deionized water, 14 ppt artificial seawater and 14 ppt York River water. Concentration units are mg/L.

	<u>Deionized Water</u>	<u>Artificial Seawater</u>	<u>York River Water</u>
MCH Conc. (\pm SD)	13.5 \pm 0.2	11.4 \pm 0.1	11.7 \pm 0.2
MN Conc. (\pm SD)	11.6 \pm 0.2	9.93 \pm 0.09	10.1 \pm 0.1
MCH/MN Conc. Ratio (\pm 90% CL)	1.16 \pm 0.03	1.15 \pm 0.01	1.16 \pm 0.02

TABLE XVII. Solubility of hydrocarbon mixtures containing o-dichlorobenzene at 20 °C.^a

<u>Component</u>	<u>Mole Fraction in Hydrocarbon Phase</u>	<u>Solubility (mg/L=SD)</u>
<u>Mixture #1</u>		
tetralin	0.6958	30.7 ± 0.7
methylcyclohexane	0.2022	3.45 ± 0.04
o-dichlorobenzene	0.1020	14.7 ± 0.3
<u>Mixture #2</u>		
tetralin	0.7029	30.8 ± 0.2
methylcyclohexane	0.2539	4.29 ± 0.07
o-dichlorobenzene	0.0432	6.48 ± 0.21

^a Pure component solubilities (mg/L ± SD) were: tetralin, 42.6 ± 0.4; methylcyclohexane, 13.2 ± 0.1; o-dichlorobenzene, 102.6 ± 0.7.

hydrocarbon phase activity coefficients for these mixtures calculated from the water solubility results and the UNIFAC group-contribution method are given in Table XVIII.

The hydrocarbon component solubilities do not appear to be significantly affected by the o-dichlorobenzene. This would be expected from the relatively low mole fraction of the o-dichlorobenzene. The UNIFAC estimated activity coefficients for o-dichlorobenzene are significantly lower than the water solubility calculated activity coefficients. The first possible reason for the lower activity coefficient value is that the UNIFAC method of estimating activity coefficients may simply be in error. The second possible reason would be that the pure compound solubility value for o-dichlorobenzene may be lower than it should be. Mackay and Shiu (1981) report an o-dichlorobenzene solubility of 145 mg/L at 25°C. The 20°C might be estimated by assuming a 5% reduction giving a value of 138 mg/L. The water solubility calculated activity coefficients for o-dichlorobenzene using this value is given in parentheses in Table XVIII. These activity coefficient values are closer to the UNIFAC estimated values. There is, otherwise, no reason to suspect the pure compound solubility for o-dichlorobenzene determined in this study to be in error.

6. Solubility of Hydrocarbon Mixtures Containing Octanoic Acid

Water solubilities of 1:1 mixtures of THN and MCH were determined to be 24.4 ± 0.3 mg liter THN and 7.46 ± 0.14 mg/l MCH. Similar measurements were made on a 1:1 THN/MCH mixture containing one percent by weight octanoic acid. This mixture was studied to determine whether

TABLE XVIII. Water solubility and UNIFAC calculated activity coefficients for hydrocarbon mixtures containing o-dichlorobenzene.

<u>Component(i)</u>	<u>Mole Fraction in Hydrocarbon Phase</u>	<u>ws $\gamma_{i(h)}$ (\pm 95% CL)</u>	<u>UNIFAC $\gamma_{i(h)}$</u>
<u>Mixture #1</u>			
tetralin	0.6958	1.04 ± 0.03	1.00
methylcyclohexane	0.2022	1.29 ± 0.02	1.23
o-dichlorobenzene	0.1020	1.40 ± 0.03 (1.04) ^a	1.17
<u>Mixture #2</u>			
tetralin	0.7029	1.03 ± 0.01	1.01
methylcyclohexane	0.2539	1.28 ± 0.03	1.19
o-dichlorobenzene	0.0432	1.46 ± 0.15 (1.09) ^a	1.20

^a Activity coefficient value if pure component o-dichlorobenzene solubility is 138 mg/L (see text.)

small amounts of surfactants that did not form micelles would affect hydrocarbon mixture solution behavior. The THN and MCH solubilities from the mixture with added octanoic acid were 24.3 ± 0.1 and 7.52 ± 0.04 , respectively. It was apparent that octanoic acid in small amounts did not alter the solubility of major components of the hydrocarbon mixture.

A series of experiments were run to determine whether the presence of 1% octanoic acid would measurably affect the rate of solution of 1:1 THN/MCH mixtures. The results of these experiments were negative.

7. Discussion

Molecular structure is important in determining the extent of deviation from ideal solution behavior for mixtures of liquid hydrocarbons. Similar components in binary mixtures exhibit ideal or nearly ideal behavior. Dissimilar components in binary mixtures exhibit significant deviations from ideality. The solubility results agree with what would be expected from published vapor-liquid equilibria results.

Multicomponent mixture vapor-liquid equilibrium is very difficult to observe since partial vapor pressures resulting from mixtures greater than two components are difficult to determine. The results of the multicomponent simulated jet fuel mixture water solubilities show that activity coefficients can be relatively easily determined from water solubility data. Chemical engineers and thermodynamicists may find aqueous solubility measurement useful to determine multicomponent mixture activity coefficients, if the components of interest are sufficiently water soluble.

The graphical, numerical (King, 1969) and UNIFAC methods of predicting multicomponent mixture activity coefficient values work reasonably well. The UNIFAC method would be the method of choice in most practical applications since only mixture composition data is required. The 'enhancement factor' concept of Leinonen (1976) for predicting multicomponent hydrocarbon mixture solubilities was not much better than the assumption of ideal solution behavior for prediction of the solubility of such mixtures. Enhancement factors are not useful, particularly in light of the ability of UNIFAC to predict hydrocarbon phase activity coefficients.

Natural levels of dissolved salts and dissolved organic material do not significantly affect the aqueous solubility behavior of liquid hydrocarbon mixtures, except for the solubility reduction due to dissolved salts. The aqueous solubility behavior using deionized, organic-free water, as used in the majority of the experiments, should therefore be applicable to natural aquatic environments.

KINETICS OF HYDROCARBON MIXTURE SOLUTION

All experiments reported up to this point have treated equilibrium conditions which are rarely encountered in environmental situations. The following experiments examine what may occur under non-equilibrium conditions. Particular emphasis has been placed on determining the mass transfer model which best explains the non-equilibrium concentrations and solution behavior.

1. Hydrocarbon Mixtures of Constant Composition

A water solution kinetics experiment was conducted using a 1-methylnaphthalene + methylcyclohexane (1:4 mole fraction ratio) hydrocarbon mixture. Three solubility vessels containing the same amount of water were equilibrated in a water bath at 20°C prior to the addition of the hydrocarbon mixture. At selected subsequent times, water samples were taken from each for analysis. The saturation concentrations were determined in a separate 48-h equilibration experiment due to insufficient water for all analyses in the same vessels. The results of this experiment are given in Table XIX.

A similar solubility experiment using an ethylbenzene + tetralin (1:3 mole fraction ratio) hydrocarbon mixture was conducted as described above. Results of this experiment are given in Table XX.

The methylcyclohexane + 1-methylnaphthalene approach-to-equilibrium experiment (Table XIX) indicated that the solute concentration ratio did not vary with distance from equilibrium and was equal to the equilibrium value. The results of this experiment can be

TABLE XIX. Methylcyclohexane (MCH)/ 1-methylnaphthalene (MN) concentration ratios for kinetic water solubility experiment using MN + MCH (0.2011 mole fraction MN) as the hydrocarbon phase.^{a, b}

<u>Time (h)</u>	<u>% of Saturation</u>	<u>[MCH]/[MN]</u> <u>($\bar{x} \pm 95\% \text{ CL}$)</u>
0.5	4	1.20 \pm 0.06
1.5	14	1.10 \pm 0.16
3	23	1.16 \pm 0.01
5	49	1.17 \pm 0.09
7	63	1.17 \pm 0.06
10	81	1.15 \pm 0.13
13	91	1.13 \pm 0.13
24	99	1.18 \pm 0.06

^aRatio at saturation = 1.20 \pm 0.04

^bSaturated MCH conc. = 14.2 \pm 0.2 mg/L; saturated MN conc. = 11.8 \pm 0.1 mg/L; as $\bar{x} \pm \text{SD}$.

TABLE XX. Ethylbenzene (EB)/ tetralin (THN) concentration ratios and solute concentrations as percent of saturation for kinetic water solubility experiment using EB + THN (0.2532 mole fraction EB) as the hydrocarbon phase.^a

<u>Time (h)</u>	<u>[EB] as % of Saturation</u>	<u>[THN] as % of Saturation</u>	<u>[EB]/[THN] ($\bar{x} \pm 95\% \text{ CL}$)</u>
1	19	17	1.54 \pm 0.07
3	55	49	1.51 \pm 0.11
5	78	71	1.49 \pm 0.17
7	92	86	1.46 \pm 0.02
12	98	98	1.35 \pm 0.11
24	100	100	1.33 \pm 0.16
48	100	100	1.36 \pm 0.02

^aSaturated EB conc. = 46.9 \pm 0.9 mg/L; saturated THN conc. = 34.6 \pm 0.2 mg/L; as $\bar{x} \pm \text{SD}$.

interpreted on the basis of a surface renewal mass transfer model in which all parcels of water have approximately the same exposure time before being replaced by turbulent exchange with the bulk water. For this situation, the average rate of mass transfer for a solute is given by Welte et al. (1984) as:

$$N_A = 2(C_{A,S} - C_{A,\infty}) \left(\frac{D_{AB}}{\pi t_{\text{exp}}} \right)^{1/2} \quad (30)$$

where, in this case, N_A is the moles of solute A leaving the surface region per unit time per unit interfacial area, $C_{A,\infty}$ is the concentration of A in the bulk water phase whose mass diffusivity is D_{AB} , $C_{A,S}$ is the aqueous concentration of A at the interface, and t_{exp} is the exposure time of a parcel of water at the water-hydrocarbon interface and isolated from the bulk water. Assumptions in the application of this model are: the interfacial boundary must be unbroken, there must be complete coverage of the surface water by the hydrocarbon phase, and t_{exp} must be sufficient for $C_{A,S}$ to be a near-equilibrium water phase concentration with respect to the hydrocarbon phase. Kinetic experiments like this can not confirm this mass transfer model because the interfacial boundary was not observed directly and turbulence was not measured. The model can be used, however, to qualitatively explain the experimental observations.

The ethylbenzene + tetralin solution kinetics results (Table XIX) are essentially the same as those for the methylcyclohexane + 1-methylnaphthalene mixture except that the concentration ratio appears to change slightly as a function of distance from equilibrium. Ethylbenzene, the more soluble component, appears to enter solution at a slightly more rapid rate. It may be that t_{exp} is not sufficient in this case for a near-equilibrium situation to be reached.

An experiment was conducted using fast and slow magnetic stirbar spinning speeds to examine if increased water phase mixing speed can cause t_{exp} to be too small for near-equilibrium to be reached at the interfacial boundary. This experiment was done at room temperature. Magnetic stirbar speeds were measured with a strobe tachometer. Laser light scattering experiments were done to determine the spinning speed that broke the water-hydrocarbon interface and caused droplets. Droplets were formed slightly above a speed of 1000 rpm, so 1000 rpm was used for the fast spinning speed. An ethylbenzene + tetralin (1:3 mole fraction ratio) hydrocarbon phase was added to the flasks while they were stirring and samples were taken at the specified times. The results of this experiment are shown in Table XXI. The solute concentration ratios were not significantly different between the fast and slow mixed vessels. The results indicate that the t_{exp} change due to the different mixing speeds was not sufficient to cause a change in the basic features of non-equilibrium solution, as indicated by essentially constant solute concentration ratios. The assumption that t_{exp} is sufficient for near-equilibrium conditions to be reached appears valid.

An approach-to-equilibrium experiment was done using a four-component hydrocarbon mixture (0.7474 mole fraction methylcyclohexane; 0.0507 mole fraction ethylbenzene; 0.1001 mole fraction tetralin; 0.1017 mole fraction 1-methylnaphthalene) at $28 \pm 1^{\circ}\text{C}$ (room temperature plus heat from magnetic stirrers). Two samples were obtained for each of the approach-to-equilibrium solute concentration determinations. Six samples were obtained for each equilibrium solute concentration determination, including those for the single component solubilities of

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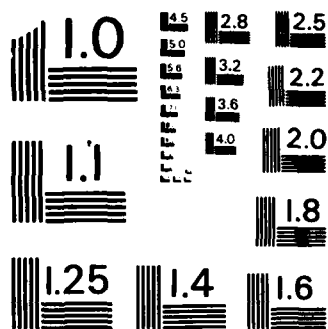
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TABLE XXI. Ethylbenzene (EB)/ tetralin (THN) concentration ratios in short-term kinetic water solubility experiment using EB + THN (0.2504 mole fraction EB) as the hydrocarbon phase at two different stirrer speeds.

<u>Time (h)</u>	<u>Slow (250 rpm)</u>	<u>Fast (1000 rpm)^a</u>
0.5	-	1.43
1	1.44	1.44
2	1.43	1.38

^aDroplets formed above 1000 rpm.

the mixture's four components. The results of the four component approach-to-equilibrium experiment are given in Table XXII. The solute concentration ratios remain essentially constant with distance from equilibrium. The single compound water solubilities at 28°C are: methylcyclohexane 13.5 ± 0.1 mg/L; ethylbenzene 178 ± 2 mg/L; tetralin 46.7 ± 0.04 mg/L; and 1-methylnaphthalene 34.7 ± 0.2 mg/L.

2. Hydrocarbon Mixture of Changing Composition

In environmental oil spill situations, the composition of the oil phase significantly alters, primarily due to evaporation. An experiment was designed to simulate the changes in the dissolution process of a hydrocarbon mixture that occur when the hydrocarbon phase composition varies due to evaporation.

a. Materials and Methods

The water solubility vessel design used is shown in Figure 16. The vessel is a 45 cm x 15 cm Pyrex cylinder with an aluminum plate cover sealed with silicone rubber. The aluminum plate was drilled and tapped for two O-ring seals holding Pyrex tubes for sample removal, inlet and outlet for N₂ gas and septum fitting. Sample tubes were located to collect water at 6 cm below the hydrocarbon phase - water phase interface and at 2 cm from the vessel bottom to provide representative sampling of the water phase. The initial composition of the hydrocarbon phase was the same as the four-component mixture reported in the preceding section. Initial volumes of water and hydrocarbon mixture were 6.5 L and 200 ml, respectively. Mixing was done with a 2.5 cm x 0.5 cm magnetic stir bar rotating at 150 rpm. The

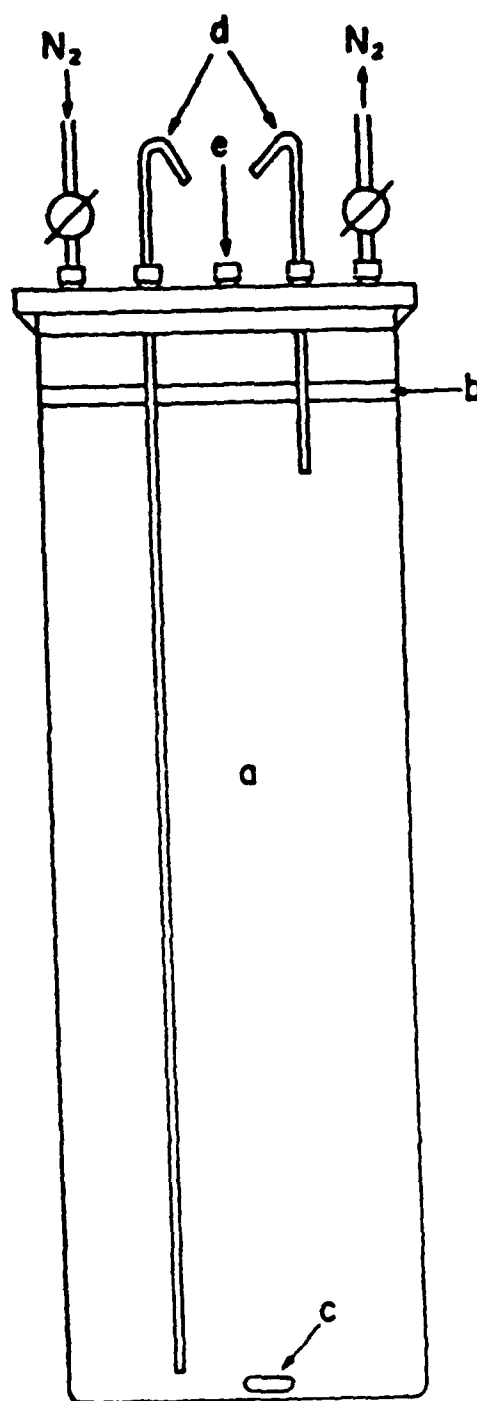


Figure 16. Water solubility vessel used in experiment in which the hydrocarbon phase composition changed due to evaporation. a - aqueous phase; b - hydrocarbon phase; c - magnetic stirbar; d - water sampling tubes; e - removable septum fitting.

Table XXII. Aqueous phase concentrations (mg/L) in a kinetic water solubility experiment using four-component hydrocarbon mixture (0.7474 mole fraction methylcyclohexane, MCH; 0.0507 mole fraction ethylbenzene, EB; 0.1001 mole fraction tetralin, THN; 0.1017 mole fraction 1-methylnaphthalene, MN).

<u>Component</u>	<u>1 Hour</u>	<u>3 Hours</u>	<u>6 Hours</u>	<u>48 hours (Equilibrium)</u>
MCH	1.16 (0.32) ^a	5.40 (0.32)	8.53 (0.31)	10.5 (0.31)
EB	1.18 (0.32)	5.50 (0.32)	8.71 (0.32)	10.4 (0.31)
THN	0.63 (0.17)	2.95 (0.17)	4.77 (0.17)	6.00 (0.18)
MN	0.70 (0.19)	3.25 (0.19)	5.27 (0.19)	6.77 (0.20)

^aNumbers in parentheses are normalized fractions of total hydrocarbon concentration at specified time.

hydrocarbon phase - water phase interface was not disturbed by the stirring action. The vessel was maintained at $28 \pm 1^\circ\text{C}$. A 500 ml/min N_2 headspace purge was maintained, except during sampling, when the N_2 valves were closed.

At each sampling time, a water sample was obtained from each sampling tube by applying pressure through the septum and a hydrocarbon phase sample (approximately 0.1 ml) was obtained by pipette through the septum fitting with septum temporarily removed. The hydrocarbon phase was diluted in pentane and analyzed by gas chromatography with flame ionization detection.

b. Results and Discussion

The hydrocarbon phase composition as a function of time is shown in Figure 17. The hydrocarbon phase composition changed as expected from the vapor pressures of the components. The methylcyclohexane mole fraction decreased rapidly and approached zero by 50 h. The ethylbenzene mole fraction increased due to the decreasing methylcyclohexane contribution up to 30 h then decreased to near zero by 121 h. The 1-methylnaphthalene mole fraction increased more rapidly than tetralin's until 72 h, at which point the tetralin mole fraction started to decrease.

The hydrocarbon concentrations in water resulting from contact with a hydrocarbon phase of changing composition should be interpretable in terms of the hydrocarbon phase composition if the surface renewal mass transfer model holds. The hydrocarbon solute concentrations as a function of time are given in Figure 18. The solute concentrations are the averages of the results from the upper

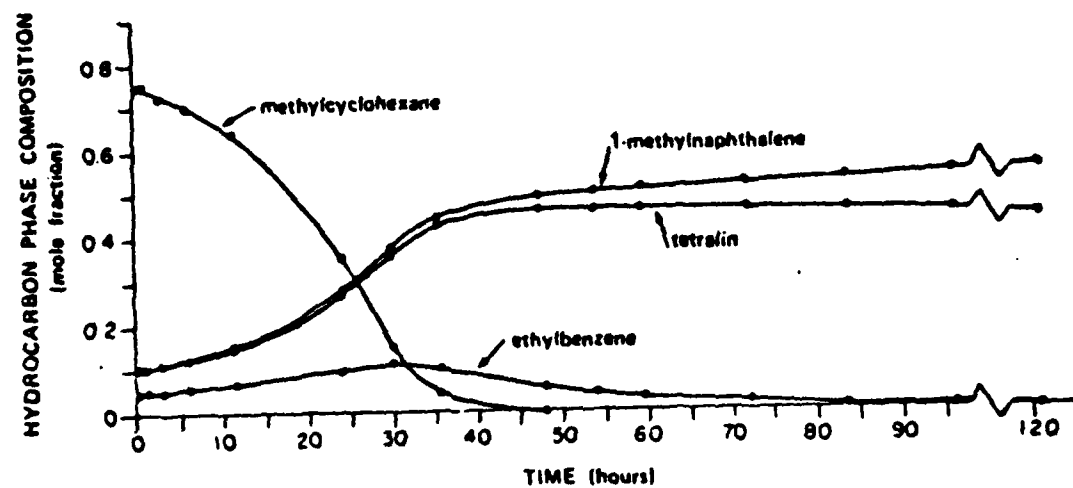


Figure 17. Hydrocarbon phase composition as a function of time.

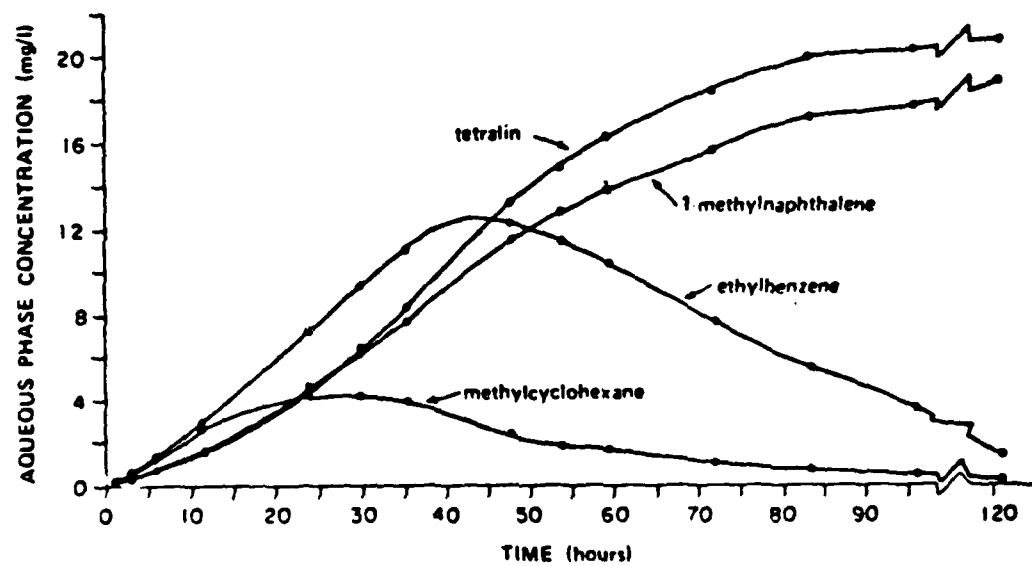


Figure 13. Hydrocarbon concentrations in the aqueous phase as a function of time.

and lower sampling tubes. Values generally agreed within 10% between the two tubes, indicating a well mixed water phase. Figure 19 shows the hydrocarbon solute concentrations (C_i) as a percent of their equilibrium concentration (C_i^*) for the hydrocarbon phase composition existing at each sampling time. Measured $x_{i(h)}$ and C_i^O data along with $\gamma_{i(h)}$ values determined as described below were used in equation (2) to calculate C_i^* values at each sampling time. Note C_i^* and C_i^O can be used as generalized concentration terms for $x_{i(w)}$ and $x_{i(w)}^O$ in equation (2).

$\gamma_{i(h)}$ values for the initial hydrocarbon phase composition were determined using equation (2) with C_i^* data in Table XX along with $x_{i(h)}$ and C_i^O values. Within the precision of water solubility measurements these are expected to be good $\gamma_{i(h)}$ estimates. All other $\gamma_{i(h)}$ values were calculated by modifying values predicted by the UNIFAC method. UNIFAC determined activity coefficients ($\gamma_{i(h)}^u$) can have significant errors. These errors (f_i) were determined using $\gamma_{i(h)}^u$ values and solubility determined $\gamma_{i(h)}$ for the initial hydrocarbon phase composition:

$$f_i = \left(\frac{\gamma_{i(h)} - 1}{\gamma_{i(h)}^u - 1} \right)_{\text{initial composition}} \quad (31)$$

$\gamma_{i(h)}^u$ values were then corrected using the following equation:

$$\gamma_{i(h)}^u(\text{corr}) = f_i (\gamma_{i(h)}^u - 1) + 1 \quad (32)$$

The hydrocarbon solute concentration ratios (see Figure 18) were essentially the same as found in the equilibrium situation for the initial hydrocarbon mixture composition during the first 11.5 h. This was expected since the hydrocarbon phase composition did not change much until after 11.5 h. The solute proportions changed substantially after this time. The methylcyclohexane solute concentration reached a

maximum around 24 h. This was expected since Figure 19 shows that methylcyclohexane became saturated with respect to the hydrocarbon phase at about 26 h. Once a component is oversaturated with respect to the hydrocarbon phase, it will tend to return from the aqueous phase to the hydrocarbon phase and be available for removal by evaporation. Similarly, the ethylbenzene solute concentration reached a maximum at about 43 h. This maximum occurred because ethylbenzene became saturated with respect to the hydrocarbon phase at about 43 h as shown in Figure 19.

The initial hydrocarbon mixture activity coefficients for tetralin and 1-methylnaphthalene were 1.28 and 1.91, respectively, but by 48 h they were both essentially unity. The effect of this change in activity coefficient values is seen in the ratio of 1-methylnaphthalene and tetralin solute concentrations, which was fairly constant up to about 30 h. After 30 h the 1-methylnaphthalene concentration decreased relative to tetralin since both activity coefficients were approaching unity. This observation is in agreement with the surface renewal mass transfer model.

It would be difficult to scale and apply these results to a particular petroleum discharge situation because of differences in non-equilibrium initial conditions, turbulent air and bulk water flows, the complexity of petroleum and the loss of hydrocarbon solutes through the air-water interface when petroleum does not cover the entire water surface. Some information, however, can be gained from these experiments which is helpful in elucidating the fate of spilled oil in the aquatic environment. A mixture of liquid hydrocarbon components will dissolve and evaporate in a fashion similar to that observed here,

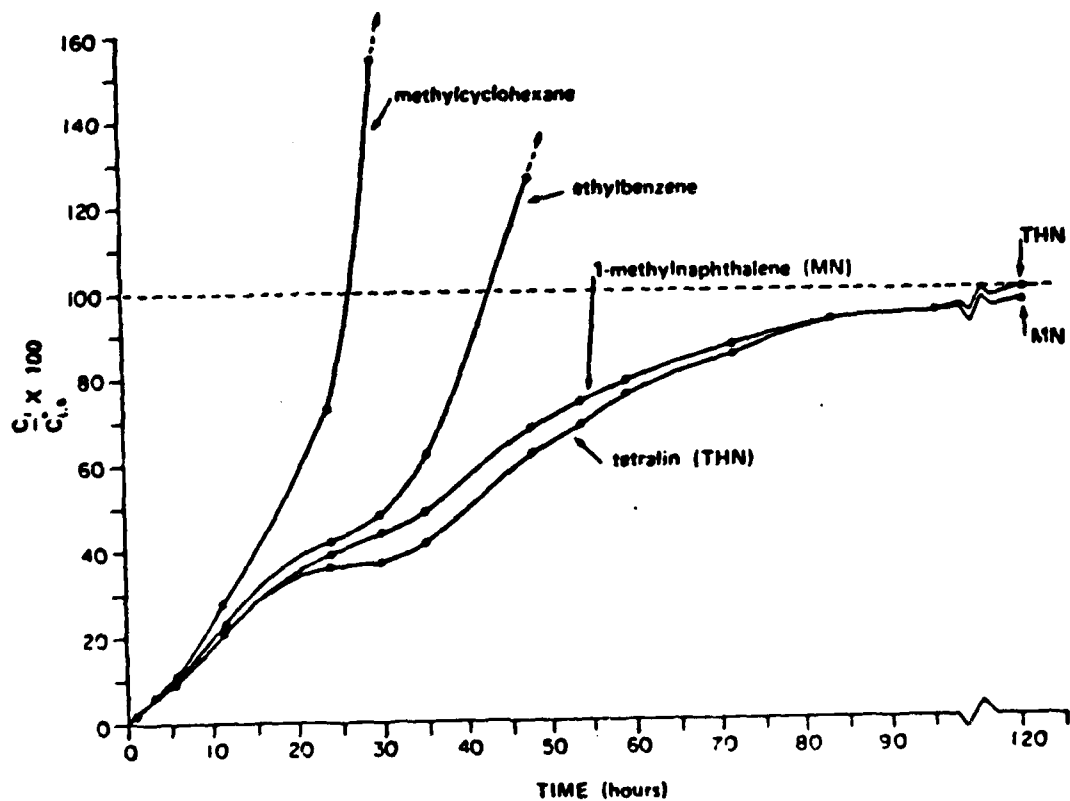


Figure 19. Hydrocarbon concentrations in the aqueous phase, as a percent of saturation concentration with respect to the hydrocarbon phase composition, as a function of time.

assuming an unbroken hydrocarbon-water interface. Hydrocarbon transport from the hydrocarbon phase to the aqueous phase appears to follow a surface renewal model. Hydrocarbon phase composition and interactions and their variation with time are important factors in controlling the aqueous phase concentrations.

3. Summary

Non-equilibrium solute concentrations resulting from water in contact with a liquid hydrocarbon mixture yields solute concentration ratios that are essentially the same as those found under equilibrium conditions, assuming the hydrocarbon phase composition does not change substantially in the process. A surface renewal mass transfer model appears to best explain these results. The essence of the surface renewal model is that small parcels of water near the hydrocarbon-water interface reach a near-equilibrium state with respect to the hydrocarbon phase prior to being mixed by turbulence with the bulk water. The bulk water then has the same solute concentration ratios as found in the equilibrium situation.

The surface renewal mass transfer model can be used to help explain solute concentrations resulting from a water + hydrocarbon mixture + vapor phase system in which the hydrocarbon phase composition changes due to evaporation.

Although it would be very difficult to accurately model and predict aqueous phase concentrations resulting from an environmental petroleum spill situation, the kinetic experiments reported here provide insights on processes occurring in a real oil spill situation.

CONCLUSIONS

The experimental design for determining the water solubility of liquid hydrocarbon mixtures (i.e, use of the solubility vessel in Figure 3 with solvent extraction followed by gas chromatographic analysis) proved to be adequate. The extraction efficiency for 1-methyl-naphthalene was at least 90%. The coefficient of variation for a set of six replicate extractions and analyses was in the range of 1 to 3%.

Hydrocarbon phase activity coefficients (at 20 and 70°C) for binary hydrocarbon mixtures determined from static vapor pressure measurements using the method of Barker, 1953 and from water solubility measurements using equation (2) were not significantly different. This finding indicates that there is no measurable decrease in component activity coefficients in the aqueous phase, in contradiction to Leinonen and Mackay, 1973 and Leinonen, 1976. It also indicates that the presence of water in the hydrocarbon phase (up to approximately 0.015 mole fraction water at 70°C) is not a significant parameter at these temperatures for medium molecular weight hydrocarbons. Equilibrium component aqueous phase concentrations resulting from liquid hydrocarbon mixture phase in contact with water, within the precision of water solubility determinations, follow the relationship in equation (2).

Molecular structure plays an important role in determining the extent of deviation from ideal solution behavior for mixtures of liquid hydrocarbons. Dissimilar components (e ., aliphatic + aromatic) in

binary mixtures exhibit significant deviations from ideality. The extent of deviation from ideality for n-alkane + aromatic binary mixtures increases as the n-alkane chainlength decreases, most likely due to increasing S^E with increasing chainlength. Departure from ideality for aliphatic + aromatic binary mixtures is greater for naphthalene aromatic components than for benzene-type components. As the aliphatic portion of the aromatic component is increased, the departure from ideality tends to decrease for the naphthalene compounds.

The problem central to predicting multicomponent liquid hydrocarbon mixture solubilities is one of adequately predicting the component activity coefficients in the hydrocarbon phase. Although several methods for predicting multicomponent mixture activity coefficients are available, the use of the UNIFAC group-contribution method appears to be the most practical since only mixture composition data is required. Predicted solubilities using UNIFAC predicted activity coefficients were generally within 10% of the measured solubilities for the multicomponent simulated jet fuel mixtures examined.

Natural levels of dissolved salts and dissolved organic material do not significantly affect the aqueous solubility behavior of liquid hydrocarbon mixtures, except for the solubility reduction due to dissolved salts.

Non-equilibrium solutions resulting from water in contact with a liquid hydrocarbon mixture have solute concentration ratios that are essentially the same as those found under equilibrium conditions, assuming the hydrocarbon phase composition does not change

substantially in the process. A surface renewal mass transfer model can be used to explain this result. The model can also be used to explain solute concentrations resulting from water in contact with a hydrocarbon phase of changing composition.

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